Gold Plating in the Electronics Industry

A REVIEW OF THE FOURTH SYMPOSIUM OF THE AMERICAN ELECTROPLATERS' SOCIETY

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Predictably enough at a meeting devoted to plating in the electronics industry, gold plating figured prominently at the Fourth Symposium on this theme held by the American Electroplaters' Society in Indianapolis, no less than 11 out of a total of 24 papers dealing with various aspects of this subject. Of these, four were concerned with applications in the semiconductor and microelectronics field, two with the requirements of gold plating for use on sealed reed relay contacts, three with processes and coating properties in the more general context of electrical contact applications, and two with analytical methods for the determination of metallic impurities or organic contaminants in plating baths.

A common factor was the preoccupation with coating properties in relation to particular applications as affected by operational parameters, compositional variations and plating solution contaminants, reflecting the increasing specificity and control of coating characteristics demanded by today's electronics industry. The concern felt over the recent rise in the price of gold was also evident; of the various approaches to the problem of off-setting the resulting cost increases, selective plating which limits the gold coating to operational areas only, and the general improvement in deposit characteristics such as porosity, hardness and wear resistance to permit the use of thinner gold deposits, were accorded little more than passing general reference.

Two papers were, however, concerned with a third possibility, namely the replacement of pure gold by alloy gold deposits of relatively low gold content. Such coatings have been used for many years in the plating of watch cases, where the requirements in terms of wear resistance and corrosion protection over long periods are not dissimilar to those of engineering applications, but though successful use in the electrical and electronics field has been documented in a number of cases in Europe, this type of coating has been more generally viewed with some suspicion on the general grounds of anticipated difficulty in compositional control and the possible effect of the presence of significant amounts of base metals on oxidation and corrosion resistance, particularly at elevated temperature.

The fourth approach to the problem, the replacement of gold by an alternative metal which could match its unique combination of properties in terms of corrosion and oxidation resistance, low and stable electrical contact resistance, high conductivity, good solderability and weldability, seems very distant of realisation. Indeed, E. F. Duffek, of Chemline Industries, Santa Clara, in a general review of the semiconductor and microelectronics field, reported increased usage of gold, notwithstanding the price rise, and attributed this to a market trend toward consumer products as opposed to military and strategic items, again emphasising the need for low cost production.

Semiconductors and Microelectronics

The paper by Duffek on "The State of Gold Plating in the Semiconductor and Microelectronics Industry" ranged widely over processes and applications. Here the main interest is in soft high-purity golds which facilitate chip bonding (die attachment) and wire bonding. These are specified in MIL-G-45204B as Type I (99.7 per cent gold) and Type III (99.9 per cent gold), with maximum hardness of 90 KHN, generally associated with high purity. It was pointed out that harder high purity golds (up to 190 KHN) were available, but the need was stressed for evaluation of their effects on device assembly, particularly wire bonding, in individual cases. Alloy gold are not favoured on grounds of instability and variation in properties.

The author then briefly reviewed the gold plating systems available, including acid (pH 3.5 to 4.5), mild acid (pH 4.5 to 6.5), neutral (pH 5.0 to 8.0), alkaline phosphate and cyanide (pH 8.0 to 11.0), non-cyanide (sulphite, pH 6.0 to 11.0), and high speed processes. The acid systems give excellent adhesion to metals and are extensively used as 'strikes' but are least tolerant to heavy metal and organic contamination. The neutral baths are superior in this respect, and show an additional advantage in minimising the effects of bipolarity which may occur in barrel plating, tending to dissolve gold or basis metal from anodic areas on non-contacting parts. Hence barrel plating is more uniform, with associated cost reduction

possible in meeting minimum thickness specifications. Non-cyanide systems are similar in tolerance to heavy metals and offer good throwing and levelling power but, according to the author, are more sensitive to operating conditions and composition. Deposits are harder than 90 KHN, and must, therefore, be evaluated for die and wire bonding as recommended earlier. The optimum pH is 9.5 but reference was made to recently developed solutions of this type that are claimed to deposit pure gold at a pH of 6.0.

Co-deposition of contaminants, leading to substandard deposits that may show defects such as discolouration on heating, increased porosity, surface residues and roughness at device assembly, testing or soldering, was cited by Duffek as a main problem area in gold plating for semi-conductor applications, a problem that has been alleviated, but not completely solved, by a general change from low pH to neutral solutions.

The remainder of this paper was devoted to the description of typical gold plating procedures, thicknesses and testing methods in the context of semiconductor device assembly in various package types, both hermetic (e.g. metal cans, ceramic dual-in-line packages (DIPs), flatpaks) and plastic-encapsulated, the latter being used mainly where costs are to be minimised and hermetic sealing is not required, as in industrial and commercial applications. The author also discussed selective plating of lead frames, emphasising that, although the cost of gold usage could be drastically reduced by techniques such as mechanical or photoresist masking, jet plating and brush plating, the expenses of proprietary machines warranted their use only in high volume production. A typical continuous strip plating cycle was described, utilising current densities of 150 to 1500 A/ft^2 to provide a throughput of from 5,000 to 15,000 units per hour. Gold plating on semiconductors for interconnect purposes was also discussed and exciting developments were forecast in this field, including the plating of entire circuit patterns on devices, die attachment and lead bond areas, and the building up of circuit patterns by plating to carry more power and permit wireless assembly. The author concluded by pointing out the need for more work on selective plating, gold solder alloys, and control problems.

Other contributions in this area were more concerned with investigational work on specific problem areas of the technology. Under this heading were papers by D. R. Johnson (Sandia Laboratories, Albuquerque, New Mexico) on "The Contribution of Plating Variables to Thermocompression Bond Quality"; by M. V. Davis (Bendix Corporation, Kansas City) on "Characteristics of Co-deposited Polymeric Material in Gold Electroplate: Its Effect on Manufacture of Electronic Assemblies"; and by K. R. Newby (Bell Laboratories, Murray Hill) on "Selective Gold Plating of Platinum and Palladium Substrates".

Johnson's paper covered a straightforward investigation of four proprietary gold plating solutions, namely, bright alkaline sulphite, acid citrate, citrate-phosphate, and cobalt-alloyed acid bright, operated under normal recommended conditions, with specific reference to the effects of deposit purity, thickness and hardness on the strength of lead frame thermocompression bonds, as evaluated by a 90° peel test, both before and after thermal ageing. The effect of a nickel undercoat of various thicknesses was also studied. The lead frame material was CDA 194, a copper alloy with nominal 2.3 per cent iron and 0.12 per cent tin, bright-annealed before plating to meet a Knoop hardness of 100 maximum. The acid citrate bath was shown to provide more consistent and higher strength bonds than the sulphite solution, and within the thickness range studied (approximately 75 to 250 micro inch) bond strength increased with gold thickness. Improved strength was also favoured by omission of the nickel underplate, despite which there was no clear indication of bond degradation in thermal ageing.

In his paper on the co-deposition of polymeric material, M. V. Davis adopted a rather broad definition of the term 'polymer' to include all non-metallic occlusion and gaseous reaction products generated at the cathode during electrolysis of gold cyanide solutions and codeposited with the plate. Here the main practical concern was with the effects of polymer codeposition on component solderability.

Eight types of plating solution were included in this study, as listed below, operated over a current density range of 1 to 10 A/ft^2 in rack and barrel plating.

		pH
A	Non-cyanide, inorganic brightener	10 to 11
B	Acid cyanide, cobalt brightener	3.5 to 4.0
C	Acid cyanide, inorganic brightener	4.0 to 4.5
D	Acid cyanide, inorganic brightener	3.8 to 4.3
E	Acid cyanide, no brightener	4.0 to 5.0
F	Alkaline cyanide, silver brightener	10.5 to 11.5
G	Neutral cyanide, inorganic brightener	6.2 to 6.8
H	Neutral cyanide, organic brightener	6.2 to 6.8

In examining coatings for polymer, the basis metal was dissolved in nitric acid and the isolated foil treated with dilute aqua regia while observing under a low power microscope. Polymeric residues were readily observed, and could be studied in more detail by stereoscopic examination of the dried specimen at 400× under polarised light. In form, they were either dense or translucent when present in small amounts and generally retained the shape of the initial gold fragment. Polymer from acid electrolytes

was web-like in structure while that from the alkaline bath F was heavy looking (it was suggested in discussion that this might in part comprise silver chloride). There was no evidence of the brown or orange colour reported by other workers.

As might be expected, less polymer was found at low current densities where there was less evolution of hydrogen, and the least amount was present in deposits from the non-cyanide solution, in this case barely discernible as a web-like residue. Barrel plated coatings showed greater volume and density of polymer than rack plated coatings under the same nominal conditions, probably due to the wide fluctuations of current density in the former case.

Vacuum fusion analysis showed considerable amounts of gas to be present in coatings, increasing with increase of current density, and in the presence of hardeners. High levels of stress were also noted by the X-ray back-reflection method in deposits from bath F on Dumet lead wires which showed poor solderability, while on similar components bath H, containing no free cyanide, produced soft gold plate which revealed no polymer on dissolution and soldered readily. The author concluded that poor solderability was attributable solely to the presence of polymer in gold plate and considered the problem sufficiently serious to raise doubts concerning the continued use of cyanide baths in plating parts that require to be soldered. Barrel plating of small electronic components in this type of solution was not recommended when solderability was a requirement.

K. R. Newby reported the successful outcome of an investigation aimed at simplifying the titanium/platinum (palladium)/gold metallisation process for producing interconnections and beam leads in the manufacture of sealed junction beam lead integrated circuits. A commonly used procedure involves successive deposition of titanium and platinum layers by sputtering or evaporation, followed by the application of a photoresist, and etching in aqua regia to remove platinum from all but the areas to be gold plated. The resist is then removed, the exposed titanium oxidised in hot nitric acid, and a second resist applied to the oxide surface to define the gold pattern prior to gold plating. The process would be simplified, with elimination of one masking stage, if resist could be applied directly to the platinum layer with sufficiently good adhesion. The degree of underplating (plating of gold under the resist) is the critical factor affecting pattern definition at the final gold plating stage, and this was used as the criterion in assessing the degree of success achieved in a study of various oxidation treatments of the platinum, and the effect of variables in resist processing and gold plating, aimed at the desired end.

It was found that anodic oxidation of platinum in N_2-purged 1N sulphuric acid for one minute at 0.2 mA/cm^2 reduced the degree of underplating, but did not eliminate it. In addition, careful control of resist processing factors, particularly of the development and post-bake stages, was necessary. The effect of variations in gold plating process and compositional parameters was studied using the following reference electrolyte with asymmetric A.C.

$KAu(CN)_2$	20 g/l
$K_2HPO_4 3H_2O$	40 g/l
KH_2PO_4	10 g/l
pH	7

Variation of gold concentration and current density were reported to have little effect on underplating, while an increase in pH to 10 gave some improvement. The most striking effect was associated with the concentration of phosphate buffer, with a marked increase in underplating when this was increased in the range from 25 to 200 per cent of the reference level while maintaining the same buffer ratio. It was hypothesised that the very small degree of underplating at the lower phosphate content was probably associated with reduction in throwing power of the solution due to the lowering of conductivity.

Using a gold bath at pH 10, with the 25 per cent phosphate level, and incorporating results from the resist processing study, the improved procedure was successfully applied to a 64-bit polar memory device with a previous history of non-adherent gold deposits and severe underplating problems.

Reed Switch Contacts

Papers dealing with aspects of gold plating in the reed switch field were presented by T. A. Davies and P. Watson, of Plessey's Allen Clark Research Centre, and by E. T. Eisenmann, of Bell Laboratories, Columbus, Ohio. In their contribution on "Potassium Inclusions in Gold Electrodeposits: Their Influence on Reed Relay Contact Behaviour", the first two authors illustrated defects in cobalt-hardened acid gold deposits on nickel-iron blades associated with faults in the starting material, including the presence of burrs from stamping, residual abrasive particles from deburring, and surface bubbles resulting from outward diffusion of impurities, mainly silicon associated with manganese and magnesium, during heat treatment, emphasising the need for material of the highest purity and surface quality for successful production plating. A number of stereoscan photomicrographs were also shown to illustrate the changes in surface topography of coatings as affected by variations in such factors as cobalt concentration, pH and current density. In

the absence of the cobalt-complex brightener and buffering agent, deposits showed outward growing spikes, with transition to a fibrous type of growth dominated by citrate rather than phosphate ions. With 0.1 g/l of cobalt, at pH 4.2, the fibrous structure was retained at intermediate current densities (0.75 and 2 A/dm^2) but coatings were nodular at either end of the current density range studied (0.25 and 5 A/dm^2). Increase in cobalt concentration to 1 g/l at the same pH gave smooth deposits over the whole of the range.

The potassium content of deposits was determined by microprobe analysis over a range of cobalt concentrations and it was demonstrated that this could be affected significantly by plating variables. Thus with 1 g/l of cobalt in the electrolyte, the potassium content of coatings could vary from 0 to 0.32 per cent depending on current density, pH and temperature. X-ray micrographs indicated that the potassium was uniformly distributed, but could not distinguish between bulk and grain boundary in-incorporation due to the small grain size of deposits.

The effect of potassium inclusions in favouring lateral spread of erosion due to arcing on "make" was discussed in terms of a general mechanism postulated for contact materials consisting of a bulk element of relatively high electronic work function, with conventional contact properties, and a uniform surface dispersion of a low work function material, e.g. potassium. At closure of contacts arc discharge is initiated at surface protrusions where electrons are more readily released due to localised high electrical field strength. In the case of a single contact material, the discharge at a particular site causes roughening, with formation of additional protuberances, hence subsequent discharges are likely to occur in the same area leading to localised deep erosion. When a material of low electronic work function is present, initial arc discharge will again occur at protrusions but low work function sites in these will be eliminated by volatilisation and the next discharge will occur at the next highest protrusion and so on, leading to lateral spread of erosion. This effect was confirmed in experiments in which gold alloy deposits known to give poor life-load characteristics in testing were treated in a boiling saturated sodium chloride solution to leave a film of salt crystals over the surface. In switching a 100 mA, 50V resistive load, there was improved lateral spread of erosion and a smaller increase in contact resistance, notwithstanding that the surface distribution of crystals achieved by this rather crude method was far from ideal.

Eisenmann in his paper on "Dependence of Selected Properties of Hard Gold on Eight Plating Variables" presented results of two series of factorially designed experiments to investigate the effect of operational parameters (current density and temperature) and compositional variables (gold content, phosphate content, concentration of uncomplexed cobalt and of cobalt EDTA complex, pH, and contamination) on surface texture, hardness, thickness distribution, and blistering tendency of cobalt hardened gold coatings for miniature reed relay contacts, to permit more precise definition of process requirements with respect to the avoidance of the most prominent types of failure, i.e. excessive contact resistance, and sticking.

Thickness was measured by coulometric stripping, and hardness by scratch testing, using a Vickers diamond with 1 g load and measuring scratch width on a scanning electron microscope at 5,000×. Surface texture was quantified for purposes of statistical evaluation as the percentage of visually bright reeds in a batch, and blistering in terms of the time required to initiate blistering of coatings on a hot stage microscope with filament temperature of 500°C. Detailed discussion of the results presented by the author in terms of positive or negative effects of individual variables, and interactions between these, on deposit characteristics of interest, is beyond the scope of the present review. Practical conclusions, however, were that for satisfactory deposition of hard gold in this application, the following variables must be precisely controlled:

Current Density:	not greater than 10 mA/cm^2
Gold Concentration:	approximately 5 g/l.
Cobalt: Gold Ratio:	preferably greater than 0.2 when Co is added as Co EDTA complex.
Temperature:	slightly above ambient, 30 to 35°C.

These conditions are consistent with those, which, according to Davies and Watson's results, would produce a smooth surface topography.

Processes and Properties in General

The paper by A. Korbelak and J. King, of Handy and Harman, New York, on "Gold Plating Today's and Tomorrow's Electronic Components" presented contact resistance and analytical data in support of two new proprietary gold plating processes, designated as "E" and "KK" respectively. In the case of the former solution, the improvement over conventional types of solution with cobalt or nickel hardeners was in its ability to furnish a stable hardener content of 0.2 to 0.3 per cent in deposits despite variations in operating parameters, within certain limited ranges, e.g. temperature 80 to 135°F, current density 5 to 20 A/ft^2, and cobalt concentration in the electrolyte of up to 4.5 times the normal operating concentration. Solution "KK" was designed to produce bright coatings with good elevated temperature stability. Comparative contact resistance measurements were presented over the load range of 10 to

200 g indicating no change in this respect for the proprietary coating after heating for 64 hours at 250°C, whereas this treatment resulted in infinite resistance in the case of conventional cobalt and nickel hardened deposits.

In the contribution from F. I. Nobel, D. W. Thomson and J. M. Leibel, of Lea Ronal, on "An Evaluation of 18 and 24 Kt Hard Gold Deposits for Contact Applications", the authors reviewed various approaches to the problem of minimising gold usage. The use of an 18 Kt gold coating would offer immediate savings of one-third in gold, while a hard 24 Kt coating would also be of interest if sufficiently ductile to permit forming of components after plating, since this would allow savings by design changes in methods of manufacture. In this context the paper presented an extensive comparison of properties of applicational importance for proprietary gold coatings of 24 Kt (99.99 per cent gold) and 18 Kt (75 per cent gold, 18 per cent copper, 7 per cent cadmium), with those of a typical cobalt-gold deposit.

The 18 Kt Coating was superior to cobalt-gold in as-plated hardness and ductility, and comparable in porosity, wear resistance and solderability. With a nickel barrier layer, only slightly higher contact resistance was exhibited after heating. Particularly striking was the marked increase in elongation after annealing, with a retained hardness of over 200. As expected, the 24 Kt high purity coating showed good contact resistance properties, but relatively poor wear capabilities without lubrication, the chief feature of the deposit being its remarkably high ductility. On the strength of this evaluation useful fields of application were foreseen for both types of coating.

Again in the context of gold savings, the paper by D. G. Foulke and R. Duva, of Sel Rex, offered a concise review of processes and properties for six binary gold alloy systems, namely, 60 to 80 per cent gold-copper, 75 per cent gold-silver, 75 per cent gold-cadmium, 80 per cent gold-nickel, 80 per cent gold-palladium, and 65 per cent gold-tin, for the general guidance of potential users, with particular reference to density, hardness, chemical resistance, wear resistance, stress and electrical properties. All of the systems mentioned were either in industrial use or under evaluation at the present time.

Analytical Methods

Of two papers on analytical aspects, one, by V. M. Leroy and A. J. Lincoln of Engelhard Minerals and Chemicals on "A Common Matrix Spectrographic Method for the Determination of 12 Elements in 10 Types of Gold Plating Solution" dealt specifically with gold plating, describing a d.c. arc spectrographic method for the determination of aluminium, silver, arsenic, cobalt, chromium, copper, iron, nickel, lead, silicon, tin and zinc in potassium gold cyanide, gold cyanide and cyanide-free gold plating solutions. The other, by H. F. Bell, of I.B.M., Poughkeepsie, on "Applications of Differential Pulse Polarography" dealt with the use of this technique for the determination of small amounts of organic additives. Of particular interest in relation to gold plating was the description of a procedure for the extraction and estimation of the hydrogen cyanide tetramer, diaminomaleonitrile, which has been postulated as being the form of organic contaminant resulting from the electrolysis of gold cyanide solutions. However, when the procedure was applied to a cyanide-citrate bath which was giving coatings of poor bondability, no tetramer was found, although deliberate doping of a new bath with the material indicated that it was detectable at concentrations as low as 5 p.p.m. This observation raises obvious questions concerning the formation mechanism and the role played by the tetramer in polymer codeposition, and the analytical technique described was seen as a useful tool in further investigations of these aspects.

Dropwise Condensation of Steam on Gold Surfaces

Steam can condense either as discrete drops or—more usually—as a continuous film, but dropwise condensation gives greatly improved heat transfer. It has been known for some time that a gold surface can promote dropwise condensation, and a recent paper in this journal by Dr Robert A. Erb of the Franklin Institute (*Gold Bulletin*, 1973, **6**, (1), 2) showed that gold plated condenser tubes offer the possibility of reductions in both the size and the cost of plant for the distillation of sea-water and even—with further development work—for power generation.

A further contribution to this subject from D. G. Wilkins, L. A. Bromley and S. M. Read of the University of California (*Am. Inst. Chem. Eng. J.*, 1923, **19**, (1), 119) tends to show, however, that dropwise condensation on solid gold tubes is dependent on the presence of minute amounts of organic compounds which have the effect of promoting a non-wetting surface. In the absence of such promoters a pure gold surface will quickly revert to filmwise condensation. Among the organic compounds found to be effective when injected in very small amounts into the boiler were lauryl mercaptan, *n*-octadecyl mercaptan and tetrakis octadecylthiosilane.

The greater success obtained with gold-plated condenser tubes is attributed to the presence of organic molecules emanating from the brightening agents present in normal commercial gold baths, but it was found that after many hours of condensing the brightener is leached out of the surface layer and the dropwise condensation fades to filmwise condensation provided no other organic molecules reach the surface.