The invention relates to a bath for the electrolytic deposition of bondable fine gold coatings having a gold content of more than 99.9% by weight, containing gold as an alkali metal or ammonium gold(I) cyanide and phosphonic acids and/or phosphoric acid or salts or derivatives thereof and a water-soluble bismuth compound.

Electroplating gold baths are used for many different purposes. In most cases they contain alkali metal or ammonium gold(I) cyanide and more rarely gold(III) cyanides or alkali metal gold sulphites.

Gold baths for decorative applications almost always deposit gold alloys with considerable proportions of alloy metal in order to produce the desired colour effect.

Gold baths for the deposition of gold with good electrical and mechanical properties as a material for use in electrical low-current contacts are common. These baths are used in the weakly acid pH range (pH 3 - 5). The coating usually contains small proportions (0.1 - 1%) of nickel, cobalt or iron as well as gold.

In addition, electroplating gold baths for the deposition of fine gold layers with gold contents of at least 99.9% are also required, as bondable coatings in semiconductor engineering, for instance.

Bonding techniques include those processes in which, in microelectronics, system supports are electrically connected to electronic components, e.g. chips, via fine wires (usually made from gold or aluminium). The wire is connected to the gold-plated bond pad using pressure and elevated temperature, frequently assisted by ultrasonic energy.

This bond connection can only be perfectly achieved if the gold coating on the bond pad is very pure (fine gold with a gold content of at least 99.9%), soft (maximum hardness 120 HV) and silky matt. Hard, high-gloss coatings are not suitable. Further requirements for the bondable gold layers are the result of the stress due to thermal tests which are performed in order to ensure good bondability. Such thermal tests are performed on e.g. unbonded test specimens, wherein, for example, no discoloration of the gold layer should occur after 5 minutes' exposure in air at 500°C. In other tests, the bonded test specimen is subjected to variable temperature tests or is subjected to air at a temperature of 150 - 180°C for several hours. These thermal tests result in diffusion processes between the gold and the support material in the gold layer. The effect of such diffusion processes on the bonding behaviour depends on the thickness of the gold layer and on its structure. Since the thinnest possible layer of gold is required, for economic reasons, the structure of the coating must be optimised by means of additives to the bath and the selection of suitable deposition conditions in such a way that a minimum thickness of gold ensures perfect bondability. Such bath additives have hitherto been known in the form of arsenic, thallium or lead.

A further criterion for the economic viability of an electroplating process is the rate of deposition from the bath while maintaining the functional requirements of the coating. The rate of deposition is the result of the current density applied and its upper limit should be as high as possible without producing losses in the desired properties of the gold layers.

Simple possibilities for producing higher permissible current densities are increasing the gold content of the bath or rapid motion of the electrolyte. The economic viability of the process suffers if the gold content is too high, due to the high price of gold.

The use of apparatus (special electroplating cells) with partial very vigorous movement of the electrolyte by streaming over or spraying onto the goods to be electroplated often also ensures, by applying masks, selective localisation of the gold plating on the functionally important surface elements of the goods. However, a high rate of flow through the electrolyte is crucial for the rate of deposition (maximum permissible current density).

Despite the increase in rate of deposition which can be achieved with these measures, a further increase in current density and rate of deposition by improving the gold baths is very desirable, wherein increased demands on the stability of the electrolyte results from the high current densities to be applied (cathodic and in particular anodic) and from the violent turbulence in the baths in flow units.

EP-OS 0 126 921 describes a bath for the electrolytic deposition of gold alloys which in addition to alkali metal gold(I) cyanide and phosphonic acids, also contains between 10 mg and 100 g/l of bismuth in the form of a water-soluble complex compound. This bath, which functions at a pH of 6 to 13, deposits pink to violet coloured alloy coatings for decorative purposes, with gold contents of 65 to 85% by weight, which are completely unsuitable for bonding applications.

A gold bath for semiconductor applications according to JP-OS 56 084 495 contains 2 to 16 g of gold as cyanoaurate, 5 to 200 g/l of citric acid, 5 to 100 g/l of phosphoric acid, 10 to 150 g/l of ammonium sulphate and 0.01 to 40 mg/l of titanium, cerium, lead, antimony, arsenic, bismuth and/or tellurium at a pH of 4 to 7. These baths are thus operated in the weakly acid range and have the disadvantage that the citric acid reacts with nickel and copper as substrate materials and intermediate layers, which leads to

contamination of the bath. Therefore these baths are not optimally suitable for bond connections.

Special gold layers are obtained from electroplating baths which, in addition to alkali metal gold(I) cyanide, contain hydrogen phosphates, phosphonic acids and nitrogen-containing carboxylic acids (DE-OS 35 37 283). Current densities of up to 15 A/dm^2 can be achieved with these in flow units. With normal bath motion, however, matt brown coatings are obtained at current densities greater than 1 A/dm^2 and these cannot be used for bonding applications.

US-PS 3 879 269 describes gold baths for the deposition of bondable fine gold coatings in high-speed cells. In addition to 24 - 40 g/l of gold, phosphates and carboxylic acids, these baths contain a critical amount of 2 - 12 mg/l of trivalent arsenic ions. Despite use in a high-speed cell and despite a very high gold concentration, usable coatings are only achieved up to a current density of ca. 4 A/dm^2.

Electroplating gold baths with trivalent arsenic as a grain refining additive all suffer from the known phenomenon that trivalent arsenic is oxidised to the pentavalent form, wherein this process takes place even when the bath is not being used, and at particularly high reaction rates, however, under the oxidative effects (high anodic current density, vigorous swirling-in of air) of high-speed electrolysis in flow or spray cells. Pentavalent As demonstrates no grain refining or gloss-producing effects. On the other hand the requisite and permissible concentration of trivalent arsenic is in the range of a few mg/l. Since there is no sufficiently accurate analytical method for this active component, reliable bath management cannot be guaranteed. Instability of the additive produces large variations in quality, which can only be limited in an unreliable manner by frequent performance checks and adjustments.

DE-OS 33 41 233 comprises an acid fine gold bath with an additive of 5 to 50 ppm (mg/l) of lead, which can be operated in the current density range 0.5 - 2 A/dm^2, wherein the optimum current density is 0.6 A/dm^2.

The use of thallium as a grain refiner at concentrations of 1 - 140 mg/l in gold baths with a pH in the range 7 - 13 is described e.g. in DE-OS 21 31 815. The current density range which can be applied is 0.1 - 20 A/dm^2.

Although it is known that gold coatings deposited from electroplating gold baths which contain lead or thallium as grain refining additives can be bonded perfectly in the freshly deposited state, they largely lose their resistance to being pulled off during the subsequent heat tests which are performed at e.g. 150°C for 24 hours, so that the bond frequently tears off.

Thus, it was the object of the present invention to develop a bath for the electrolytic deposition of bondable fine gold coatings having a gold content of more than 99.9% by weight, containing gold as an alkali metal or ammonium gold(I) cyanide and phosphonic acids and/or phosphoric acids or salts or derivatives thereof and a water-soluble bismuth compound, which ensures a high rate of deposition by means of applying a high current density with perfect stability of the bath, and with which good bondability and heat resistance can be achieved for the coating.

This object is achieved according to the invention in that it contains 2 to 100 g/l of gold, 0.1 mg/l to 5 g/l of bismuth, 0 to 250 g/l of phosphonic acid or salts, esters or simple substitution products thereof, and/or 0 to 250 g/l of phosphoric acid or salts thereof, wherein the sum of the amounts of phosphonic acid compounds and phosphates must be at least 5 g/l, and it has a pH of 7.5 to 10.

The baths preferably contain phosphonic acids or salts or esters thereof which have at least two groups of the form - $PO(OH)_2$, which are members of an aliphatic single or branched hydrocarbon chain which may also be interrupted by one or more nitrogen atoms.

The electroplating gold baths advantageously contain 2 to 50 g/l of gold as alkali metal or ammonium gold(I) cyanide, 0 to 250 g/l of alkali metal phosphates, alkali metal hydrogen phosphates or the corresponding ammonium salts, 5 to 250 g/l of a phosphonic acid in the form of 1-hydroxyethane-1,1-diphosphonic acid, amino-tri-methylenephosphonic acid, ethylenediamine-tetra-methylenephosphonic acid or the hexasodium salt thereof and 0.5 mg to 4 g/l of bismuth in the form of ammonium bismuth citrate.

Gold baths which contain 8 to 24 g/l of gold, 40 to 150 g/l of phosphate, 20 to 120 g/l of phosphonic acid and 0.5 to 4000 mg/l of bismuth have proven to be particularly effective.

In addition, the baths may also contain polyphosphoric acids, superphosphates, amidopolyphosphates, pyrophosphates and the conducting salts, buffer substances, complexing agents or wetting agents which are customary in electroplating.

Using the electroplating gold baths according to the invention, a deposition of bondable fine gold coatings is obtained at high current density and high rate of deposition. Using the usual materials and motion in the bath, a current density of up to 4 A/dm^2 can be used, wherein the rate of deposition is up to about 2.50 $\mu m/min$. In high-speed cells (jet-plating cells), the permissible current density is up to 25 A/dm^2, wherein rates of deposition of up to 14.5 $\mu m/min$ may be achieved.

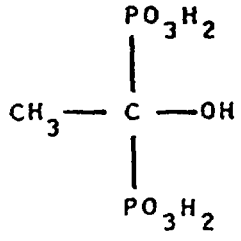
The gold coatings produced in this way are very pure (fineness 99.99%) and soft (hardness 70 - 120 HV) with a semi-gloss

finish and are outstandingly bondable. The bismuth content of the gold coating is less than 50 ppm. The fine gold coatings demonstrate excellent stability towards thermal stress, both before and after bonding. Gold coatings of 0.4 μm thickness on a nickel substrate survive the heat test involving 5 minutes exposure at 500°C without discoloration. Bonded samples demonstrate no drop in tensile strength after 48 hours exposure at 150°C. Weakening of the bond strength of coatings, observed when thallium and lead are added to the bath, does not occur.

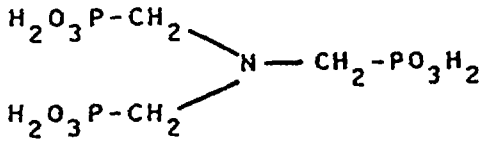
The baths are completely stable, regardless of the storage time (without being used) and of the period of use.

The phosphonic acids used in the electroplating gold baths according to the invention are preferably those which contain at least 2 groups of the form $-PO(OH)_2$ which are members of an aliphatic single or branched hydrocarbon chain, wherein this hydrocarbon chain may be interrupted by one or more nitrogen atoms. The members of the hydrocarbon chain may be substituted by NH_2 or OH groups or other simple substituents.

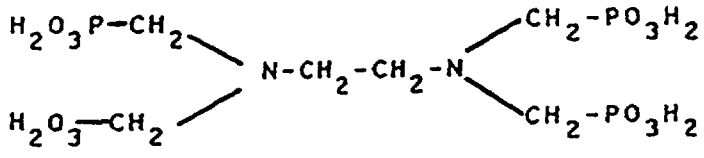
An example of a simple nitrogen-free phosphonic acid of the type mentioned, with 2 acid groups, is 1-hydroxyethane-1,1-diphosphonic acid,



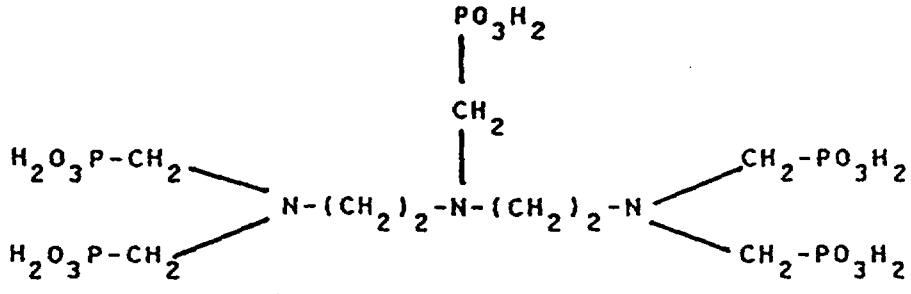
An example of a nitrogen-containing phosphonic acid with 3 acid groups is amino-tri-(methylenephosphonic acid),



An example of a nitrogen-containing phosphonic acid with 4 acid groups is ethylenediamine-tetra-methylenephosphonic acid,



An example of a nitrogen-containing phosphonic acid with 5 acid groups is diethylene-triamine-penta-methylenephosphonic acid



Bismuth may be used as e.g. ammonium bismuth citrate, but any other water-soluble bismuth compounds may also be used.

The optimum concentration of bismuth depends on the phosphonic acid being used or, when using a pure phosphate bath, on this. It may be determined by a test procedure. The amount of bismuth required increases with the number of $-PO_3H_2$ groups located on the phosphonic acid.

The following examples are intended to illustrate the baths according to the invention in more detail:

1. A gold electrolyte is prepared in the form of an aqueous solution of the following components:

   18 g/l of $KAu(CN)_2$ (= 12 g/l of Au)
   100 g/l of K_2HPO_4
   6 mg/l of ammonium bismuth citrate (= 3 mg/l of Bi).

   After adjusting the pH to 8.0 and the bath temperature to 70°C, yellow, silky matt coatings with good bondability are obtained using direct current at a current density of 0.5 - 3 A/dm^2 and a material motion of 5 cm/sec.

   The same bath provided exactly the same kind of coatings in a spray cell (jet-plating) in the current density range 0.5 - 15 A/dm^2.

   The gold coatings produced in this way are quite suitable for the intended bonding applications, but their surface finish is somewhat irregular and slightly speckled.

   If the bismuth additive is not present in the bath, then only brown, matt, coatings which cannot be used for bonding are obtained with a material motion of 5 cm/sec and current densities of more than 0.5 A/dm^2 and in a spray cell with current densities of more than 2 A/dm^2.

2. A gold electrolyte is prepared in the form of an aqueous solution of the following components:

   18 g/l of $KAu(CN)_2$ (= 12 g/l of Au)
   5 g/l of 1-hydroxyethane-1,1-diphosphonic acid
   KOH to adjust the pH to 7.5
   2 mg/l of ammonium bismuth citrate (1 mg/l of Bi).

Yellow, silky matt coatings with good bondability were obtained when using a direct current at current densities of 0.5 - 3 A/dm^2 with a material movement of 5 cm/sec and a bath temperature of 70°C.

The same bath provided exactly the same kind of coatings in the current density range 0.5 - 20 A/dm^2 in a spray cell (jet-plating) after increasing the gold content to 16 g/l.

3. A gold electrolyte is prepared in the form of an aqueous solution of the following components:

24 g/l of $KAu(CN)_2$ (= 16 g/l of Au)
100 g/l of ethylenediamine-tetra-methylenephosphonic acid
KOH to adjust the pH to 8.0
and 6 g/l of ammonium bismuth citrate (3 g/l of Bi).

The coatings produced using this bath under the same operating conditions as in example 2 correspond in appearance and quality to those in example 2.

4. To a basic electrolyte consisting of

18 g/l of $KAu(CN)_2$ (= 12 g/l of Au)
100 g/l of K_2HPO_4

is added either

60 g/l of 1-hydroxyethane-1,1-diphosphonic acid and
10 mg/l of ammonium bismuth citrate (5 mg/l of Bi) or
60 g/l of amino-tri-methylenephosphonic acid and
15 mg/l of ammonium bismuth citrate (7.5 mg/l of Bi) or
60 g/l of the hexasodium salt of
ethylenediamine-tetra-methylenephosphonic acid and
1.5 g/l of ammonium bismuth citrate (0.75 g/l of Bi) or

100 g/l of ethylenediamine-tetra-methylenephosphonic acid and 6 g/l of ammonium bismuth citrate (3 g/l of Bi).

The pH of this bath is then adjusted to 8.0 with KOH and the temperature is set at 70°C.

Under conventional conditions, i.e. with little movement of the electrolyte and a material movement of ca. 5 cm/sec, all the baths provided yellow, silky matt coatings with very uniform surface finishes using unpulsed direct current in the current density range 0.5 - 3 A/dm^2 or in spray cells in the current density range 0.5 - 25 A/dm^2.

The coatings produced from these baths had a hardness of 70 - 110 HV (Vickers hardness). The bismuth content was less than 0.005% (50 ppm). 0.5 μm thick gold coatings on a nickel substrate demonstrated no discoloration at all after 5 minutes exposure in air at 500°C. Bondability in the ultrasonic process using aluminium wire of 300 μm thickness was perfect, wherein no wires were pulled off in tensile tests up to more than 500 cm. After 48 hours exposure of bonded samples in air at 150°C, it was found that the bond strength had not decreased in the least.

Patent Claims

1. A bath for the electrolytic deposition of bondable fine gold coatings having a gold content of more than 99.9% by weight, containing gold as an alkali metal or ammonium gold(I) cyanide and phosphonic acids and/or phosphoric acid or salts or derivatives thereof and a water-soluble bismuth compound, characterised in that
it contains 2 to 100 g/l of gold, 0.1 mg/l to 5 g/l of bismuth, 0 to 250 g/l of phosphonic acid, salts, esters or simple substitution products thereof and/or 0 to 250 g/l of phosphoric acid or salts thereof, whereby the sum of the amounts of phosphonic acid compounds and phosphates must be at least 5 g/l, and it has a pH of 7.5 to 10.

2. A bath according to Claim 1,
characterised in that
it contains phosphonic acids or salts or esters thereof, which have at least two groups of the form $-PO(OH)_2$, whichare members of an aliphatic single or branched hydrocarbon chain which may also be interrupted by one or more nitrogen atoms.

* C L M S *