

[54] ELECTRODEPOSITION OF
GOLD-ANTIMONY ALLOYS AND
COMPOSITIONS THEREFOR

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75/165

[56] References Cited

UNITED STATES PATENTS

2,905,601	9/1959	Rinker et al.	204/43 G
3,020,217	2/1962	Rinker	204/43 G
3,380,814	4/1968	Cathrein et al.	204/46 G X
3,666,640	5/1972	Smith	204/44

R25,883 10/1965 Duva et al. 204/43 G

FOREIGN PATENTS OR APPLICATIONS

16,523	7/1969	Japan	204/43 G
1,547,539	10/1968	France	204/43 G
1,221,532	7/1966	Germany	75/165

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[57] ABSTRACT

A neutral and stable gold and antimony metal plating bath and gold and antimony metal alloys of outstanding properties; an electrolytic bath operated at a pH between 6.8 and 7.3 which is stable under the plating conditions for a period up to a year and longer capable of depositing from the electrolyzed solution a gold and antimony metal alloy at weight percentages heretofore producing poor deposits; codeposition as an alloy of gold and antimony metal which is suitable as a doped chip-attach surface.

4 Claims, No Drawings

ELECTRODEPOSITION OF GOLD-ANTIMONY ALLOYS AND COMPOSITIONS THEREFOR

This invention pertains to a gold alloy plating bath and a method for plating a gold alloy. More particularly, this invention pertains to a neutral and stable gold and antimony metal plating bath and gold and antimony metal alloys of outstanding properties which have been plated according to the novel method; still further, this invention pertains to an electrolytic bath operated at a pH between 6.8 and 7.3 which is stable under the plating conditions for a period up to a year and longer and is capable of depositing from the electrolyzed solution a gold and antimony metal alloy at weight percentages heretofore producing poor deposits; in accordance with the present invention, codeposition as an alloy of gold and antimony metal from a stable plating system has been disclosed which is suitable as a doped chip-attach surface.

BACKGROUND OF THE INVENTION

It has become increasingly more necessary to replace as much gold as possible in a gold electrodeposit. If by replacing part of the gold content in the deposit the properties can be improved, the reduced costs alone justify the substitution. Inasmuch as gold in a pure state deposited on a substrate has poor properties, such as displayed in the form of galling, or does not have an electrical behavior increasingly needed for various electronic devices, the emphasis has been on obtaining gold as an alloy from electrolyzed bath as a step in electroplating the desired device. Hence, obtaining an alloy of gold having improved properties is an important, or perhaps primary, consideration for searching for useful gold alloys which can be electrodeposited. Numerous patents are available in this art. Some of these patents, such as British Pat. No. 928,088, show an electrolytic bath for electrodeposition of a bright gold deposit of nickel, cobalt, or copper and other like codeposits. Although antimony has been mentioned as a codeposit, no specific bath has been disclosed with respect to the particular base metal. Still further, no deposit properties have been given, such as the amount of gold codeposit with one of the metals indicated.

A somewhat similar disclosure is found in U.S. Pat. No. 2,812,299. Antimony is not mentioned as one of the codeposited metals. Still further, U.S. Pat. No. 2,905,601 discloses various electrolytic baths, which apparently are for the purpose of codepositing, with gold, various other metals. Again, while the base metal salts have been added and indicated as capable of depositing, no specific disclosure of an antimony bath has been found and most of the disclosure is directed to a conjoint deposition of at least one base metal.

A specific disclosure concerning the deposition of gold-antimony layer on a major face of a wafer suitable for attaching a silicon chip has been disclosed in U.S. Pat. No. 2,814,589, however, no actual composition of an alloy from the bath is indicated. In this patent, no properties are set forth with respect to the deposition of antimony and no particular alloy has been recited. The claims in this patent are directed, however, to a copper overplate on gold-antimony layer. It is noted that other metals, which have been electrodeposited are recited

and include a number of metals heretofore only deposited in minute proportions with gold. Still further, the disclosed baths are generally acidic or employ hydrochloric acid known in electrochemical deposition to be a highly toxic acid. Consequently, the last mentioned patent merely illustrates what is known in the art and shows that gold alloys are obtainable.

In a summary of developments in gold alloy plating Parker, Recent Developments In Gold Alloy Plating, *Plating Magazine*, June, 1958, Pages 631-635, the doped alloys, (disclosed in some of the above patents such as U.S. Pat. No. 2,814,589), have been illustrated. However, these have been indicated as not being functionally useful in amounts greater than 0.3% antimony by weight of gold. These amounts have been alleged to be unacceptable because the alloy will fracture and break away from a device such as germanium semiconductor material. Still further, it has been alleged that antimony in amounts from 0.5 to 1% in gold alloy will make the alloy "ball up" and refuse to wet germanium when it is attempted to fuse the wafer to the plated disk.

In addition, it has been alleged that amounts greater than 1% antimony by weight in gold produce a smutty, dirty-brown plate and increasing amounts produce a non-adherent plate. Although it is alleged that the minimum amount of antimony required is not known, it has been indicated that only a few parts per billion are required for some devices such as germanium in the manufacture of germanium based transistor devices. However, it is noted that the amounts which have been used are based on a gold electrodeposit produced by an entirely different process using entirely different baths from those claimed herein.

BRIEF DISCUSSION OF THE INVENTION

It has now been found that contrary to the disclosure in the prior art, another gold bath which codeposits gold and antimony metal from a very stable plating system, i.e., solution, produces doped chip-attached surfaces of outstanding characteristics. Moreover, the bath stability, which is important for the full utilization and exhaustion of gold is outstanding and the efficiency thus unquestionably of higher order than previously illustrated in the art.

Still further, the controllable alloy composition which has often been alluded but not demonstrated in the prior art can now be accomplished over a specified range of antimony-gold alloys in the process disclosed herein and the obtained alloys have outstanding properties. Inasmuch as the bath, which has been disclosed herein, has low percent, by weight, of organic compounds, the problems associated with the deposition of an impure alloy in presence of organic compounds has been reduced or minimized, if not eliminated, and the included impurities which often contribute undesirable characteristics in the production of doped chip-attached surfaces are eliminated and/or minimized.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the invention, the bath which is suitable for electrolyzing and for depositing of gold antimony alloys of outstanding properties is as illustrated in the Table herein.

TABLE I

ALLOY GOLD PLATING BATH			
Solution Make Up	grams/liter	oz/gal	Range grams/liter
a. Potassium Phosphate* (Dibasic) $K_2HPO_4 \cdot 3H_2O$	130.0	17.4	100-200
b. Potassium Phosphate* (Monobasic) KH_2PO_4	50.0	6.7	30-60
c. Gold as $KAu(CN)_2$	12.3	1.5 troy oz.	8-17
d. Antimony Potassium Tartrate $K(SbO)C_4H_4O_6 \cdot \frac{1}{2}H_2O$	.1-1		.1-1
e. Potassium Tartrate** $C_4H_4O_6K \cdot \frac{1}{2}H_2O$	5.0	.67	5.-50
Deposit: .1 to 4% Sb in gold on basis of total weight of deposit.			

*Percent of a. to b. is 70 to 75% on hydrous basis to anhydrous basis, by weight, respectively.
**By increasing the amount of potassium tartrate as shown the amount of antimony in the deposit is decreased and vice-versa.

In accordance with the above and illustrating a further embodiment of this invention, the operation conditions for the bath are as illustrated in Table II herein.

TABLE II

ALLOY GOLD PLATING BATH		
Operating Conditions for Bath	Optimum	Range
Temperature	140°F	100-160°F
Sp Gravity (25°C)	18°Be min. (make-up gravity)	
pH (25°C)	7.0	6.8-7.3
electrometrically		
Anodes	platinum	
Agitation	moderate to vigorous	
ASF (amperes/ft ²)	10	1-25 5-20 (preferred)

In accordance with a further embodiment, the alloy gold plating bath was used to deposit the necessary electrodeposits, which are acceptable industrial deposits and not mere jewelry deposits displaying only decorative properties based on mere surface appearance. Thus, in accordance with the above, a chip attach surface was formed of a gold-antimony alloy on a printed circuit board having an underlying electroless copper coating, and an electrolytic copper or nickel deposit appropriately masked by depositing on the board, by immersion, completion of the circuit, electrolysis of the bath and rinsing. The alloy deposit is also used on lead frames, i.e., as surface deposits for attaching transistor devices to nickel, nickel-iron, copper, etc., metals, such as deposited electrolytically.

It is emphasized herein that the invention is directed especially to the gold bath which is stable at the above optimum operating conditions for at least a year. The bath is a unique neutral gold-antimony bath which produces controllable amounts of gold and antimony alloy of coherent structure having outstanding functional properties, i.e., providing a specific junction layer which will not switch the transistor device by a stray or extraneous background bias.

In accordance with the above-identified invention, stability of the bath has been defined as producing no visible precipitate of either the antimony compound and/or the gold compound and when the bath is evaporated to ¼ of the original volume and brought back up to the original dilution, it will show essentially no precipitates.

- What is claimed is:
- 25 1. An electrolyte for electrodeposition of a gold antimony alloy from an aqueous solution at a pH of 6.8 to 7.3 consisting essentially of (a) dibasic potassium phosphate, from 100 to 200 grams/liter, (b) monobasic potassium phosphate, from 30 to 60 grams/liter, potassium tartrate, from 5 to 50 grams/liter, gold as KAu_2 , from 8 to 17 grams/liter, and antimony potassium tartrate, from .1 to 1 grams/liter and wherein a to b is 70 to 75% on hydrous basis to anhydrous basis, by weight, respectively.
- 30 2. A method for electrodepositing an antimony gold alloy which comprises electrolyzing an aqueous solution by impressing a current between anode and a workpiece as a cathode, said solution consisting essentially of potassium phosphate (dibasic), from 100 to 200 grams/liter, potassium phosphate (monobasic), from 30 to 60 grams/liter, potassium tartrate, from 5 to 50 grams/liter, gold as KAu_2 , from 8 to 17 grams/liter, antimony potassium tartrate, from 1. to 1 grams/liter, wherein the specific gravity of said solution at 25°C is 18°Be and the pH at 25°C as determined electrometrically is from 6.8 to 7.3 and depositing said alloy on said workpiece.
- 40 3. The method as defined in claim 2, wherein the anode is platinum anode and wherein during the deposition, the solution is agitated.
- 45 4. A composition for use to make an electrolyte for the electrodeposition of a gold-antimony alloy consisting essentially of potassium phosphate (dibasic), potassium phosphate (monobasic), potassium gold cyanide, antimony potassium tartrate, and potassium tartrate, wherein the potassium phosphate (dibasic) to potassium phosphate (monobasic) is 70 to 75 percent on hydrous basis to anhydrous basis, by weight, respectively.
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