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(54) High speed method for plating palladium and palladium alloys

(57) A high speed method of depositing palladium and palladium alloys is disclosed. The high speed method uses an aqueous, ammonia-based bath which has reduced free ammonia in the bath. The high speed method may be used to deposit palladium and palladium alloy coatings on various substrates such as electrical devices and jewelry.

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Description

[0001] The present invention is directed to high speed methods for plating palladium and palladium alloys using ammonia-based palladium and palladium alloy plating compositions. More specifically, the present invention is directed to high speed methods for plating palladium and palladium alloys using ammonia-based palladium and palladium alloy plating compositions where the level of free ammonia is reduced.

[0002] The dramatic increase in the price of gold over the past several years has given rise to new methods and equipment in the metal plating field and attempts to use substitute metals such as palladium and its alloys through, for example, reel-to-reel plating. The use of such plating processes requires high speed plating and high speed requires current densities of 10 Amps/dm^2 and above. In addition, the industry desires high speed plating to achieve metal deposition in as short a time as possible to be more efficient in the manufacturing of metal plated articles. High speed plating equipment may employ the jet plating principle where the plating solution is sprayed out onto a substrate being plated with a jet stream to provide vigorous agitation. Vigorous agitation may also be supplied without the jet stream by moving the solution very rapidly past the substrate being plated by use of a pump or by moving the substrate rapidly through the solution. Another form of high speed plating is selective plating. Such selective plating uses specialized plating equipment such as chemical or mechanical masks which limit metal deposits to specific required areas while leaving other areas free of the metal.

[0003] Attempts have been made to plate palladium and its alloys from high speed plating equipment with various baths; however, the deposits are either burned or matte gray or they are bright to semi-bright and highly stressed and exhibit surface micro-cracks which are visible only under a microscope at high power. Such cracks can be visible in the deposit right out of the plating bath or they become visible later after the deposit has been permitted to stand at room temperature for a day or more. There is a large amount of literature about the cracks. It is attributed to the co-deposition of hydrogen with palladium. After the hydrogen is emitted from the deposit, the cracks appear. The industry desires palladium and palladium alloy deposits that are crack-free at usable current densities in high speed plating from 10 to 100 Amps/dm^2 and higher. In addition the industry desires palladium and palladium alloys which have high wear resistance, high corrosion resistance, low electrical resistance and good solderability, such as for use as coatings for electrical contacts.

[0004] To achieve a palladium or palladium alloy deposit from a plating process with the desired properties, a number of process parameters must be addressed. Such parameters include, but are not limited to, the composition of the bath, bath temperature, agitation rate during plating and bath pH. The specific parameters to achieve an optimum process may vary widely depending on whether the process is for low speed or high speed plating. Many palladium and palladium alloy plating processes use ammonia as a ligand for metals. Ammonia based processes have many advantages over ammonia free processes. Such advantages include: 1) no detrimental decomposition products from organic ligands in contrast to other types of ligands, such as polyamine type ligands; 2) highly ductile deposits; and 3) palladium-ammonia salts are more economical and readily available than many exotic palladium salts which are required for ammonia free processes.

[0005] Such ammonia-based processes operate from the low acidic to high alkaline pH range, such as from a pH of 6 and higher. During bath operation free ammonia escapes from the baths as ammonia vapor. This alters the pH of the bath and destabilizes it to seriously compromise the bath performance. This is especially problematic at high speed plating where plating rates are faster and bath agitation is more vigorous than with low speed plating, thus causing a greater rate of free ammonia loss. Also, plating at high temperatures or an increase in temperature during plating, which is typical for high speed plating, causes ammonia loss from the bath, thus destabilizing the plating process. Ammonia-based plating processes require periodic replacement of ammonia to maintain the stability and optimum operation of the process. Typically, free ammonia levels are kept at 50 g/L to 150 g/L, more typically 100 g/L. However, ammonia replenishment is difficult. Ammonia is often replenished by adding ammonium salts, e.g. ammonium sulfate for sulfate-based solutions, to the plating bath; however, this results in an accumulation of anions in the plating bath which dramatically reduces the life of the bath due to salting out of bath components. Ammonia gas and ammonium hydroxide also may be added to the baths; however, such compounds are inconvenient and problematic to handle. Both present potential serious noxious and toxic hazards to workers using them. The more free ammonia added to the bath the greater the ammonia loss, thus presenting a hazard to the environment. Accordingly, the industry desires a high speed plating method where the free ammonia level is reduced.

[0006] At high speed plating, such as reel-to-reel plating, ammonia loss is greater, thus requiring a greater rate of ammonia replacement and increasing the difficulty of maintaining a stable plating process. Also, the high temperatures and rapid agitation of the bath during high speed plating further increase the loss of ammonia and destabilize the bath. A rapid loss of ammonia results in an unstable bath and poor process performance. This reduces the overall efficiency of the process and increases the cost of plating.

[0007] U.S. 5,415,685 discloses an ammonia-based palladium plating composition and process. The patent alleges that the ammonia-based palladium plating composition is both stable and provides a whiter palladium deposit over a wider range of plating thicknesses than conventional processes. The process described in the patent is a low speed process with current densities ranging from 0.1 Amps/ft2 to 50 Amps/ft^2 (0.01 Amps/dm^2 to 5 Amps/dm^2). Such processes are not suitable in an industry where high speed plating is mandatory to achieve economic efficiency. Accordingly, there is a need for a high speed method for plating palladium and palladium alloys from an ammonia-based bath.

[0008] In one aspect a method includes: a) providing a composition consisting essentially of one or more sources of palladium, ammonium ions and urea; b) contacting a substrate with the composition; and c) generating a current density of at least 10 Amps/dm^2 to deposit palladium on the substrate.

[0009] In another aspect a method includes: a) providing a composition consisting essentially of one or more sources of palladium, one or more sources of alloying metals, ammonium ions and urea; b) contacting a substrate with the composition; and c) generating a current density of at least 10 Amps/dm^2 to deposit a palladium alloy on the substrate.

[0010] The high speed methods provide stable palladium and palladium alloy baths and eliminate the need to add ammonium sulfates, ammonium hydroxide, ammonia gas or other ammonium compounds to replenish the free ammonia levels in the bath. Thus, the hazards and other disadvantages of adding such compounds to the plating baths are eliminated. The high speed methods also reduce the amount of free ammonia in the bath in contrast to many conventional high speed palladium and palladium alloy processes. Accordingly, the vapor level of ammonia is reduced.

[0011] The high speed methods provide bright, ductile and crack free palladium and palladium alloy deposits on substrates at high current densities. The high speed methods may be used to plate palladium and palladium alloys on any substrate where palladium and palladium alloy coatings are desired. Such substrates include electronic components as well as jewelry. Electronic components may include electrical contacts where high wear resistance, high corrosion resistance and low electrical contact resistance and good solderability are desired.

[0012] As used throughout the specification, the following abbreviations have the following meaning unless the context clearly indicates otherwise: °C = degrees Centigrade; g = gram; mg = milligrams; L = liter; mL = milliliter; Amp = amperes; dm = decimeter; μm = microns = micrometer; and rpm = revolutions per minute.

[0013] The terms "depositing", "plating" and "electroplating" are used interchangeably throughout this specification. The term "burnt" means a dull or coarse finish. The term "bright" means an optical reflective finish. The term "ductile" or "ductility" is the resistance of metal deposits to cracking during distortion, such as bending or stretching. "Metal turnover (MTO)" = total palladium deposited in grams divided by the palladium content in the solution in grams. All amounts are percent by weight unless otherwise noted. All numerical ranges are inclusive and combinable in any order except where it is logical that such numerical ranges are constrained to add up to 100%.

[0014] The methods are high speed electroplating methods for depositing palladium and palladium alloys with low levels of free ammonia, thus reducing the generation of ammonia vapor during high speed electroplating and vigorous bath agitation. Typically, the free ammonia in the electroplating baths is less than 50 g/L. The reduction in free ammonia also provides for a more environmentally friendly bath since less ammonia vapor is generated during electroplating in contrast to many conventional ammonia-based baths. The unpleasant and annoying odor of ammonia is eliminated or at least reduced. Also, constantly evaporating ammonia causes considerable difficulties in controlling the pH value. In conventional ammonia-based baths ammonia is continuously added in metered quantities to maintain an optimum pH. Typically, ammonium sulfate, ammonium hydroxide and ammonia gas are used. Such compounds are difficult to handle are noxious and are hazardous to workers. Further, adding such compounds to the baths often cause the salting out of bath components, thus compromising bath performance. The high speed methods eliminate the need to add such compounds to the plating baths.

[0015] Urea is included in the baths to stabilize the baths by compensating for the reduced free ammonia and for preventing changes in the pH due to the loss of ammonia. The high speed electroplating baths have a pH range of 6 to 10, typically, from 7 to 8. Including urea in the baths eliminates the need to replenish ammonia by the addition of ammonium compounds or ammonia. Urea is easier to handle than ammonia or ammonium compounds. Urea is a weak complexing agent and addition of large quantities of urea to ammonia-based plating baths does not detrimentally affect the microstructure of palladium and palladium alloy deposits. Further, there is no accumulation of decomposition products which limit the bath life. Additionally, one of the hydrolysis products of urea is ammonia and this ammonia is used to replenish the loss of free-ammonia and help maintain the desired pH and the bath stability. Urea is included in the baths in amounts such that the total amount of urea and free ammonia in the baths are from 100 g/L to 150 g/L.

[0016] A wide variety of palladium compounds may be used as a source of palladium in the high speed electroplating methods provided that they are compatible with the high speed process and other bath components. Such palladium compounds include, but are not limited to, palladium complex ion compounds with ammonia as the complexing agent. Such compounds include, but are not limited to, dichlorodiammine palladium (II), dinitrodiammine palladium (II), tetrammine palladium (II) chloride, tetrammine palladium (II) sulfate, tetrammine palladium tetrachloropalladate, tetramine palladium carbonate and tetramine palladium hydrogen carbonate. Additional sources of palladium include, but are not limited to, palladium dichloride, palladium dibromide, palladium sulfate, palladium nitrate, palladium monoxide-hydrate, palladium acetates, palladium propionates, palladium oxalates and palladium formates. One or more sources of palladium may be mixed together in the bath. Typically, the ammonia palladium complexes are used in the bath. Sufficient amounts of one or more sources of palladium are added to the bath to provide 10 g/L to 50 g/L of palladium for deposition, or such as from 20 g/L to 40 g/L of palladium.

[0017] Ammonia may be added to the bath by water soluble ammonium salts. Such ammonium salts include, but are not limited to, ammonium halides, such as ammonium chloride and ammonium bromides, ammonium sulfates and ammonium nitrates. Sources of ammonia are added to the baths in sufficient amounts to provide free ammonia in amounts of less than 50 g/L, or such as from 10 g/L to 45 g/L, or such as from 15 g/L to 35 g/L.

[0018] Alloying metals which may be added to the high speed electroplating baths to form palladium alloys include, but are not limited to, one or more of nickel, cobalt, iron and zinc. The alloys may be binary alloys or ternary alloys. Typically, the alloys are binary alloys such as palladium/nickel, palladium/cobalt and palladium/zinc. More typically, the binary alloy is palladium/nickel. Typically, the ternary alloy is palladium/nickel/zinc. One or more alloying metals may be added to the baths as a water soluble salt. Such salts include, but are not limited to, halides, sulfates, sulfites, phosphates, pyrophosphates, nitrates and salts with organic acids, such as acetates, propionates, oxalates and formates. Typically, the halide and sulfate salts are used. Sufficient amounts of one or more alloying metal salts are added to the baths to provide alloying metal ions in amounts of 0.1 g/L to 15 g/L, or such as from 1 g/L to 10 g/L.

[0019] Palladium alloys made by the high speed methods are stable. Stability means that the alloy composition remains substantially constant over a wide current density as well as changes in the pH of the bath, temperature fluctuations and bath agitation rates. The weight ranges ofpalladium in the binary alloys range from 50wt% to 90wt% with the balance being the alloying metal. An example of such a binary alloy which is used for coatings on electrical contacts is palladium/nickel (80wt%/20wt%). The weight ranges of palladium in a ternary alloy range from 40wt% to 80wt% with the balance being the two alloying metals in equal or unequal proportions.

[0020] The palladium electroplating baths used in the high speed methods consist essentially of one or more sources of palladium, ammonium ions, free ammonia and urea. When the bath is used for depositing a palladium alloy, one or more alloying metal ions are added to the bath. The palladium and palladium alloys deposited by the high speed methods are bright, crack free and adhere to substrates.

[0021] One or more conventional additives also may be added to the bath. Such conventional additives include, but are not limited to, buffers, brighteners, surfactants and mixtures thereof. Such additives may be included in the bath in conventional amounts.

[0022] One or more surfactants which do not compromise the performance of the bath may be included. Typically, such surfactants include, but are not limited to, non-ionic surfactants, cationic surfactants and anionic surfactants. Examples of such surfactants are polyethylene glycols, alkyl quaternary ammonium salts and sulfopropylated alkylalkoxylates.

[0023] Buffering agents include, but are not limited to, one or more of acetic acid, boric acid, carbonic acid, citric acid, tetraboric acid, maleic acid, itaconic acid and salts thereof. Other conventional water soluble acids also may be included as buffering agents.

[0024] Mineral acids and bases also may be added to the baths to help maintain the pH. Such mineral acids include sulfuric acid, hydrochloric acid and nitric acid. Bases include, but are not limited to, sodium hydroxide and potassium hydroxide. Typically, sulfuric acid or sodium hydroxide is used.

[0025] Suitable brighteners are those compounds which provide a bright palladium or palladium alloy deposit. Such brighteners include conventional organic brighteners. Such organic brighteners include, but are not limited to, succinimide, maleimide, quinolines, substituted quinolines, phenanthrolines and substituted phenanthrolines and quaternized derivatives thereof, pyridine and its derivatives, such as pyridine carboxylic acids, pyridine carboxylic acid amines, and polypyridines, such as bipyridines, nicotinic acid and its derivatives, pyridinium alkyl sulfobetaine, piperidine and its derivatives, piperazine and its derivatives, pyrazine and its derivatives and mixtures thereof. Typically, the brighteners used in the high speed baths are organic brighteners which have nitrogen containing heterocyclic rings, however, excluding aromatic sulfonamides. More typically, the brighteners used are pyridine derivatives, pyrazine derivatives or mixtures thereof.

[0026] Since the palladium and palladium alloys deposited by the high speed methods are typically crack free, stress reducing agents are, in general, excluded from the baths. An example of such stress reducing agents are the aromatic sulfonamides. A typical aromatic sulfonamide which is used as a stress reducing agent is saccharin.

[0027] Bath temperatures may be maintained by conventional heating apparatus. Bath temperatures range from 40 to 70° C, or such as from 50 to 60° C. Maintaining the bath temperature within the ranges, in particular at the higher end of the range, is highly desirable because as the temperature increases the amount of ammonia vapor leaving the bath also increases. Accordingly, temperature maintenance is important.

[0028] The high speed electroplating methods use current densities from 10 Amps/dm^2 and higher. Typically, current densities range from 10 Amps/dm^2 to 100 Amps/dm^2, or such as from 20 Amps/dm^2 to 80 Amps/dm^2. Such current densities are controlled using conventional rectifiers.

[0029] Conventional high speed plating apparatus may be used to electroplate palladium metal and palladium metal alloys. Typically, the palladium and palladium alloys are electroplated using reel-to-reel plating apparatus; however, any apparatus which maintains a high speed plating rate may be used.

[0030] Conventional insoluble anodes may be used with the high speed methods. Examples of insoluble anodes include, but are not limited to, platinized titanium, mixed oxide coated titanium and stainless steel. Also, anodes with the above mentioned materials with the shield design as described in US 2006/0124451 may be used.

[0031] Cathodes include any substrate which may be plated with palladium or a palladium alloy. In general, the palladium or palladium alloy is deposited on copper, copper alloy or nickel-plated copper substrates. Such substrates may be electrical contacts where high wear resistance, high corrosion resistance, low electrical contact resistance, high ductility and good solderability are required. Examples of an electrical contact are lead frames and electrical connectors. Electronic devices which include such electrical contacts include, but are not limited to, printed circuit boards, semiconductor devices, optoelectronic devices, electrical components and automobile components. Additionally, the high speed methods may be used to deposit palladium or palladium alloys on components for solar cell devices and jewelry as well as any article which may accept a palladium or palladium alloy coating.

[0032] The thicknesses of the palladium and palladium alloy coatings deposited by the high speed methods may vary and depend on the function of the substrate. In general, thicknesses range from 0.1 μm to 100μm. Typically, the thicknesses range from 0.5μm to 20μm.

[0033] The rate of deposit depends on the current density used. In general, the rate may range from 1μm/min to 30μm/min. For example, palladium/nickel alloy may be plated at 3μm/min at 10 Amps/dm^2 and 18μm/min at 60 Amps/dm^2.

[0034] The following examples are intended to further illustrate the high speed methods, but are not intended to limit the scope of the invention.

Example 1 (comparative)

[0035] The following conventional palladium/nickel alloy aqueous, ammonia-based composition was prepared to deposit a palladium/nickel alloy (80/20% w/w):

Table 1

COMPONENT	AMOUNT (g/L)
Palladium as $Pd(NH_3)_4SO_4$	15
Nickel as $NiSO_4$	6
Boric acid	26
Free NH_3 as $(NH_4)_2SO_4$	35
Nitrogen containing heterocyclic brightener	0.1
NH_4OH	Sufficient amount to achieve pH

[0036] The ammonia-based palladium/nickel alloy composition was added to a 1000 ml beaker with a magnetic stirrer to maintain agitation of the composition during electroplating. The anode was a platinzed titanium insoluble anode and the cathode was a brass substrate.

[0037] The temperature of the composition was maintained at 50° C and the initial pH was 7.2. Electroplating was done at a high current density of 10 Amps/dm^2. The experiment was run until 20 MTO with respect to palladium metals was achieved.

[0038] Free ammonia in the bath was analyzed every MTO for the first 5 MTOs, then reduced to a frequency of every 3 to 5 MTOs. The content of the ammonia in the bath was monitored by a pH titration method using 809 Titrando™ from Metrohm. It was observed that the bath was chemically unstable once the deposition began with the initial low free ammonia concentration of 35 g/L. Bath destabilization was noticeable by a white precipitate forming at the bottom of the beaker. In order to maintain the stability and operation of the bath and achieve a bright and ductile deposit, the white precipitate was removed from the bath by filtration, and the free ammonia content was increased to 100 g/L by adding ammonium sulfate. The strong odor of ammonia was noticeable during electroplating. Additionally, free ammonia lost during electroplating had to be replenished to maintain a stable pH. 3-4 g of ammonia as ammonia gas and NH_4OH were added to the bath per gram of palladium plated in addition to the amount of ammonia added through $Pd(NH_3)_4SO_4$ replenishment. Ammonia concentrations of 100 g/L were needed to maintain the stability of the bath. Although a bright and ductile deposit was plated, stability varied over the 20 MTO and required elimination of the white precipitate in addition to adding 3-4 g of ammonia/g of palladium plated to replenish the bath and maintain bath stability.

Example 2

[0039] The following palladium/nickel alloy aqueous, ammonia-based composition was prepared for depositing a bright and ductile palladium/nickel alloy (80/20% w/w):

Table 2

COMPONENT	AMOUNT (g/L)
Palladium as $Pd(NH_3)_4SO_4$	15
Nickel as $NiSO_4$	6
Boric acid	26
Free NH_3 as $(NH)_2SO_4$	35
Urea	100
Nitrogen containing heterocyclic brightener	0.1
NH_4OH	Sufficient amount to achieve pH

[0040] The ammonia-based palladium/nickel alloy composition was added to a 1000 ml beaker with a magnetic stirrer to maintain agitation of the composition during electroplating. The anode was a platinized titanium insoluble anode and the cathode was a brass substrate.

[0041] The temperature of the composition was maintained at 50° C and the pH was 7.2. Electroplating was done at a high current density of 10 Amps/dm^2. The experiment was run until 20 MTO with respect to palladium metal was achieved.

[0042] Free ammonia in the bath was analyzed every MTO for the first 5 MTOs then analysis was reduced to a frequency of every 3 to 5 MTOs. The content of the ammonia in the bath was monitored by a pH titration method using 809 Titrando™ from Metrohm. Urea levels were analyzed using Genesis II FTIR Spectrometer™ from Mattson Instruments. Electroplating bath analysis showed that the ammonia/ammonium level and the pH remained stable throughout the electroplating (20 metal turnover with respect to palladium). There was no noticeable white precipitate. Urea replenishment was 0.7 to 0.8 g/g of palladium metal deposited.

[0043] Using the ammonia-based/urea electroplating composition eliminated the need to replenish ammonia during electroplating with undesirable and hazardous compounds such as NH_4OH and ammonia gas. Low levels of free ammonia were easily maintained during electroplating in contrast to the bath of Example 1. Also, noxious vapors were reduced due to the low free ammonia. Additionally, the frequency and amount of urea replenishment was less than the ammonia replenishment in comparative Example 1 using NH_4OH and ammonia gas, thus providing a more economical and cost effective process than the conventional method.

[0044] This method was repeated except that the pH of the bath was 8. The results were substantially the same as at a pH of 7.2.

Example 3

[0045] The palladium/nickel method described in Example 2 was repeated except that the amount of urea added to the electroplating composition was 80 g/L. The rate of urea replenishment was 0.7 to 0.8 g/g of palladium metal deposited on the brass substrate. The bath was stable throughout electroplating. The performance of this method was the same as in Example 2. A bright and ductile palladium/nickel alloy was deposited on the brass substrate.

Example 4

[0046] The following palladium/nickel alloy aqueous, ammonia-based composition was prepared for depositing a bright and ductile palladium/nickel alloy (80/20% w/w):

Table 3

COMPONENT	AMOUNT (g/L)
Palladium as $Pd(NH_3)_4SO_4$	25
Nickel as $NiSO_4$	10

(continued)

COMPONENT	AMOUNT (g/L)
Boric acid	26
Free NH_3 as $(NH_4)_2SO_4$	35
Urea	80
Nitrogen containing heterocyclic brightener	02

[0047] The ammonia-based palladium/nickel alloy composition was added to a 1000 ml beaker. The cathode was a rotating cylinder pre-plated with bright nickel. During plating the cathode was rotated at 1000 rpm. The pH of the ammonia-based composition was maintained at 7.2 during electroplating and the temperature was 50° C. Electroplating was done at a current density of 20 Amps/dm^2. The bath was stable during the electroplating process. The palladium/nickel deposits were bright, ductile and adhered to the bright nickel.

[0048] The method described above was repeated twice with the same parameters except that they were done at current densities of 40 Amps/dm^2 and 60 Amps/dm^2. The results were the same as at 20 Amps/dm^2. Bright and ductile palladium/nickel deposits were deposited on the nickel at the high current densities and adhered to the nickel.

Example 5

[0049] Four bright nickel coated brass substrates were electroplated with the aqueous, ammonia-based palladium/nickel composition as described in Example 4. Each substrate was plated with the composition at different current densities. The current densities were 20 Amps/dm^2 40 Amps/dm^2, 60 Amps/dm^2 and 80 amps/dm^2. The pH of the plating composition was 7.2 with a temperature of 50° C. The high speed method was done using jet plating equipment designed for laboratory testing. The plating composition was applied to the substrates at a flow rate of 800 liters/hour. All of the palladium/nickel deposits on the bright nickel coated brass substrates were bright, ductile and adhered to the substrates.

Example 6

[0050] The following aqueous, ammonia-based palladium metal composition is prepared for depositing a palladium coating on a copper substrate:

Table 4

COMPONENT	AMOUNT (g/L)
Palladium as $[Pd(NH_3)_4]Cl_2$	10
Free NH_3 as $(NH_4)Cl$	30
Boric acid	20
Urea	100
Nitrogen containing heterocyclic brightener	0.2

[0051] The aqueous, ammonia-based palladium composition is deposited on the copper substrate using jet plating equipment as described in Example 5. The pH of the composition is maintained at 8 and the temperature of the composition is maintained at 40° C. The current density is 20 Amps/dm^2. The bath is expected to be stable during electroplating. The resulting palladium coatings on the substrates are expected to be semi-bright and crack-free.

Example 7

[0052] The following aqueous, ammonia-based palladium/cobalt alloy composition is prepared for depositing a palladium/cobalt alloy on a copper substrate:

Table 5

COMPONENT	AMOUNT (g/L)
Palladium as $[Pd(NH_3)_4]Cl_2$	10

(continued)

COMPONENT	AMOUNT (g/L)
Cobalt as $CoSO_4$	5
Free NH_3 as NH_4Cl	30
Urea	90
Boric acid	20
Nitrogen containing heterocyclic brightener	1

[0053] The aqueous, ammonia-based palladium alloy composition is deposited on the copper substrate using jet plating equipment as described in Example 5. The pH of the bath is maintained at 7.5 and the temperature is maintained at 60° C. The current density is 90 Amps/dm^2. The bath is expected to be stable during electroplating. The palladium/cobalt deposit is expected to be bright and crack-free.

Example 8

[0054] The following aqueous, ammonia-based palladium/zinc alloy composition is used to deposit a palladium zinc alloy on a copper/tin alloy substrate:

Table 6

COMPONENT	AMOUNT (g/L)
Palladium as $[Pd(NH_3)_4]Cl_2$	15
Zinc as $ZnSO_4$	5
Free NH_3 as $(NH4)_2SO_4$	40
citric acid	15
Urea	100
Nitrogen containing heterocyclic brightener	0.3

[0055] The aqueous, ammonia-based palladium alloy composition is deposited on the copper/tin alloy substrate using jet plating equipment as described in Example 5. The pH of the composition is maintained at 7 and the temperature of the composition is maintained at 60° C. The current density is 30 Amps/dm^2. The bath is expected to be stable during electroplating. A bright and crack-free palladium/zinc alloy is deposited on the copper/tin alloy.

Example 9

[0056] The following aqueous, ammonia-based palladium/nickel/zinc alloy composition is used to deposit a palladium/nickel/zinc alloy on a copper substrate:

Table 7

COMPONENT	AMOUNT (g/L)
Palladium as $Pd(NH_3)_4SO_4$	20
Nickel as $NiSO_4$	5
Zinc as $ZnSO_4$	1
Free NH_3 as $(NH_4)_2SO_4$	40
Urea	70
Citric acid	15
Nitrogen containing heterocyclic brightener	0.5

[0057] The aqueous, ammonia-based palladium alloy composition is deposited on the copper substrate using the jet plating equipment as described in Example 5. The pH of the composition is maintained at 7 and the temperature of the composition is maintained at 60° C. The current density is 85 Amps/dm^2. The bath is expected to be stable during electroplating. The palladium/nickel/zinc alloy is expected to be bright and crack-free.

Claims

1. A method comprising:

a) providing a composition consisting essentially of one or more sources of palladium, ammonium ions and urea;
b) contacting a substrate with the composition; and
c) generating a current density of at least 10 Amps/d_M^2 to deposit palladium on the substrate.

2. The method of claim 1, wherein the current density ranges from 10 Amps/dm^2 to 100 Amps/dm^2.

3. The method of claim 1, wherein the composition further includes one or more acids or salts thereof.

4. The method of claim 1, wherein the composition further includes one or more brightener.

5. The method of claim 1, wherein the composition has a free ammonia concentration of less than 50 g/L.

6. A method comprising:

a) providing a composition consisting essentially of one or more sources of palladium, one or more sources of alloying metals, ammonium ions and urea;
b) contacting a substrate with the composition; and
c) generating a current density of at least 10 Amps/dm^2 to deposit palladium alloy on the substrate.

7. The method of claim 6, wherein the current density ranges from 10 Amps/dm^2 to 100 Amps/dm^2.

8. The method of claim 6, wherein the composition further includes one or more acids or salts thereof.

9. The method of claim 6, wherein the composition further includes one or more brightener.

10. The method of claim 6, wherein the composition has a free ammonia concentration of less than 50 g/L.

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- US 20060124451 A **[0030]**