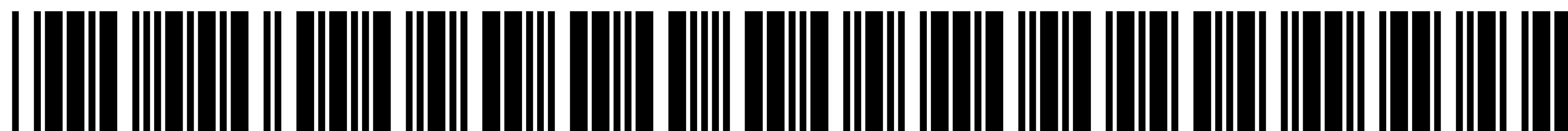
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(54) ELECTROPLATING PROCESS AND COMPOSITION

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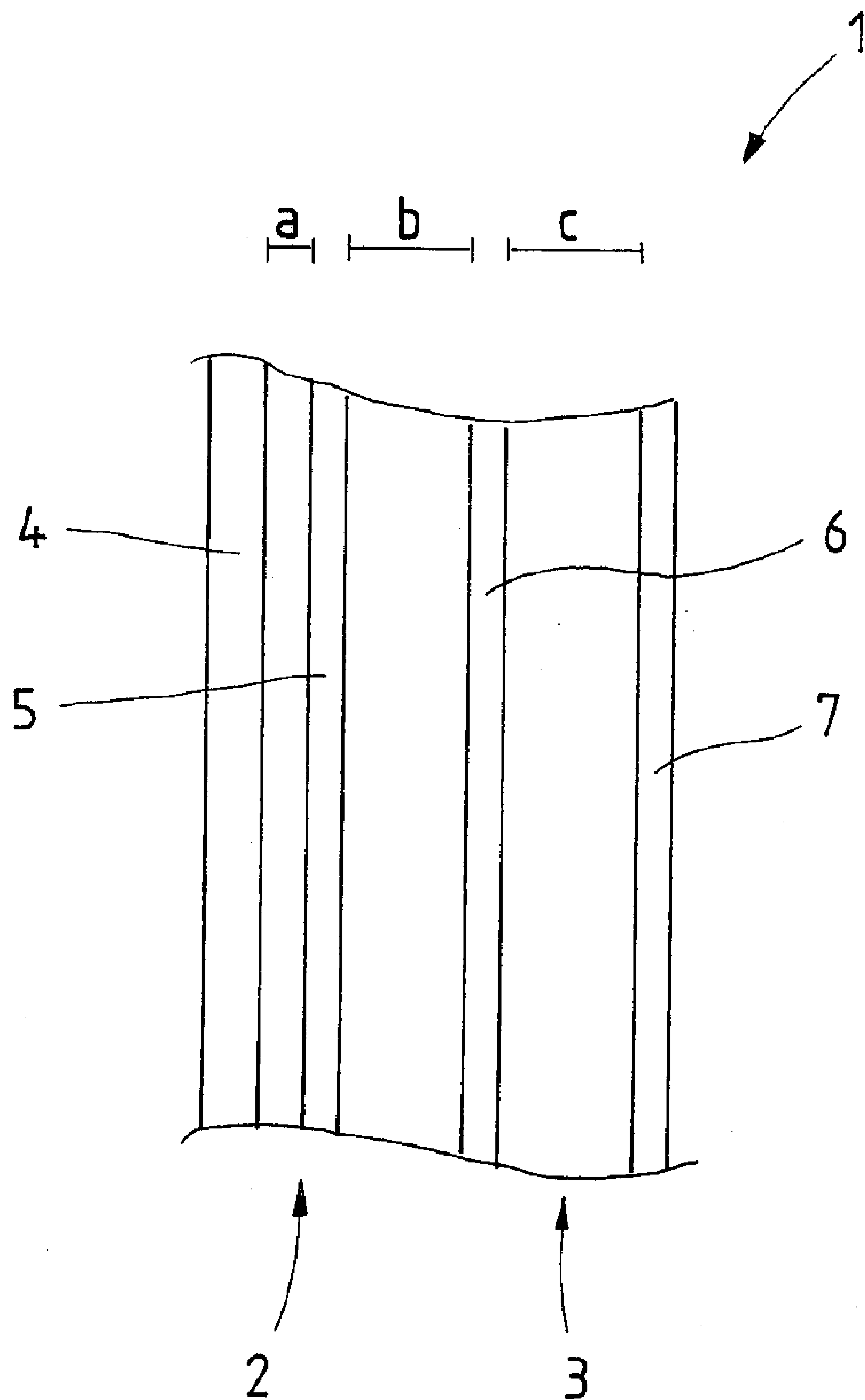
(57) ABSTRACT

A plating process employing an anode having a precious metal-based active material, and an electrolytic plating composition comprising a source of metal ions in an amount sufficient to electrolytically deposit a metal such as Cu onto the substrate, a source of chloride ions in an amount sufficient to provide at least 70 mg/L chloride ions into the composition, and a source of a d-block metal ions selected from the group consisting of molybdenum, vanadium, zirconium, tantalum, tungsten, hafnium, and titanium.



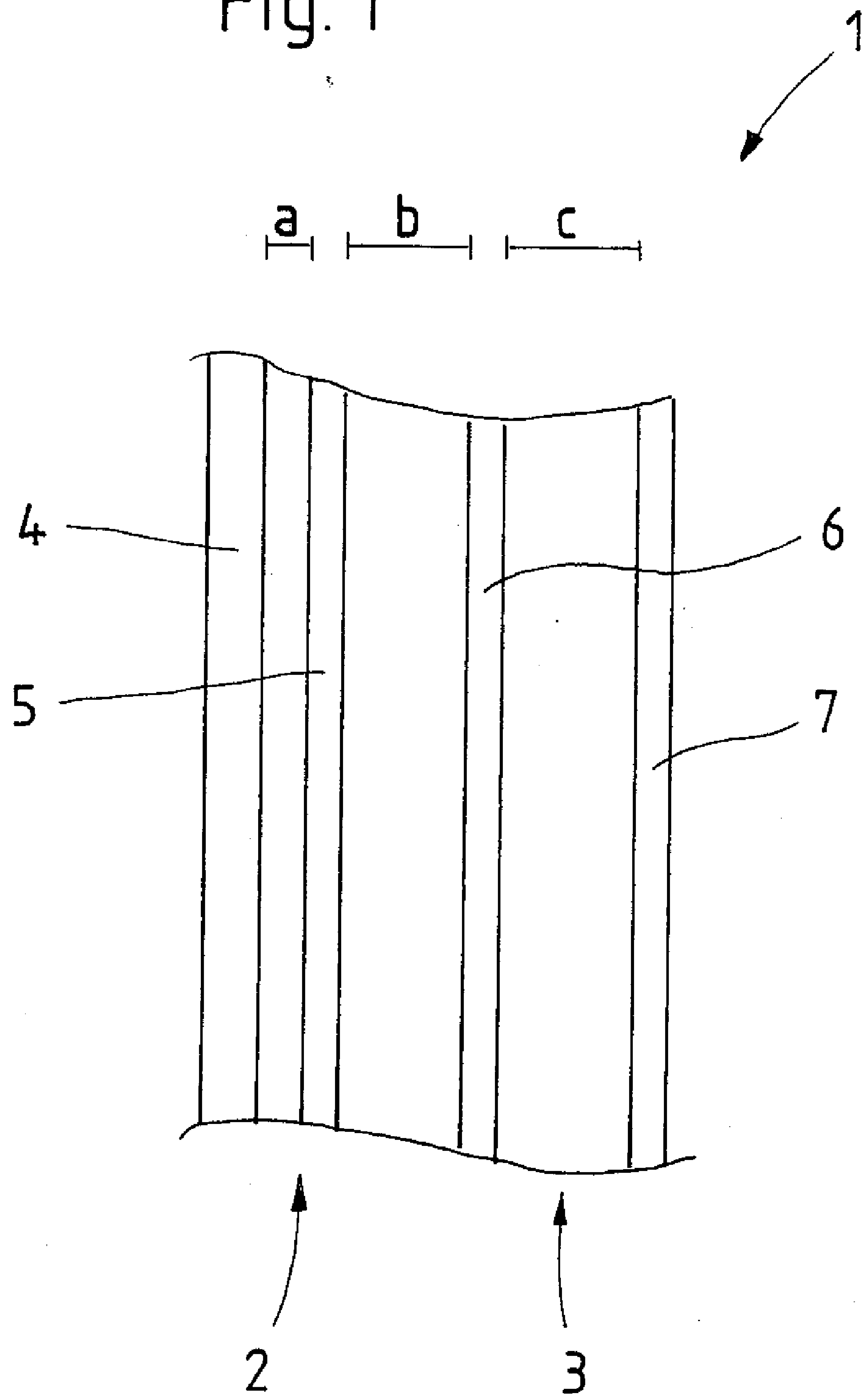


Fig. 1
1
a
b
c
4
5
6
7
2
3

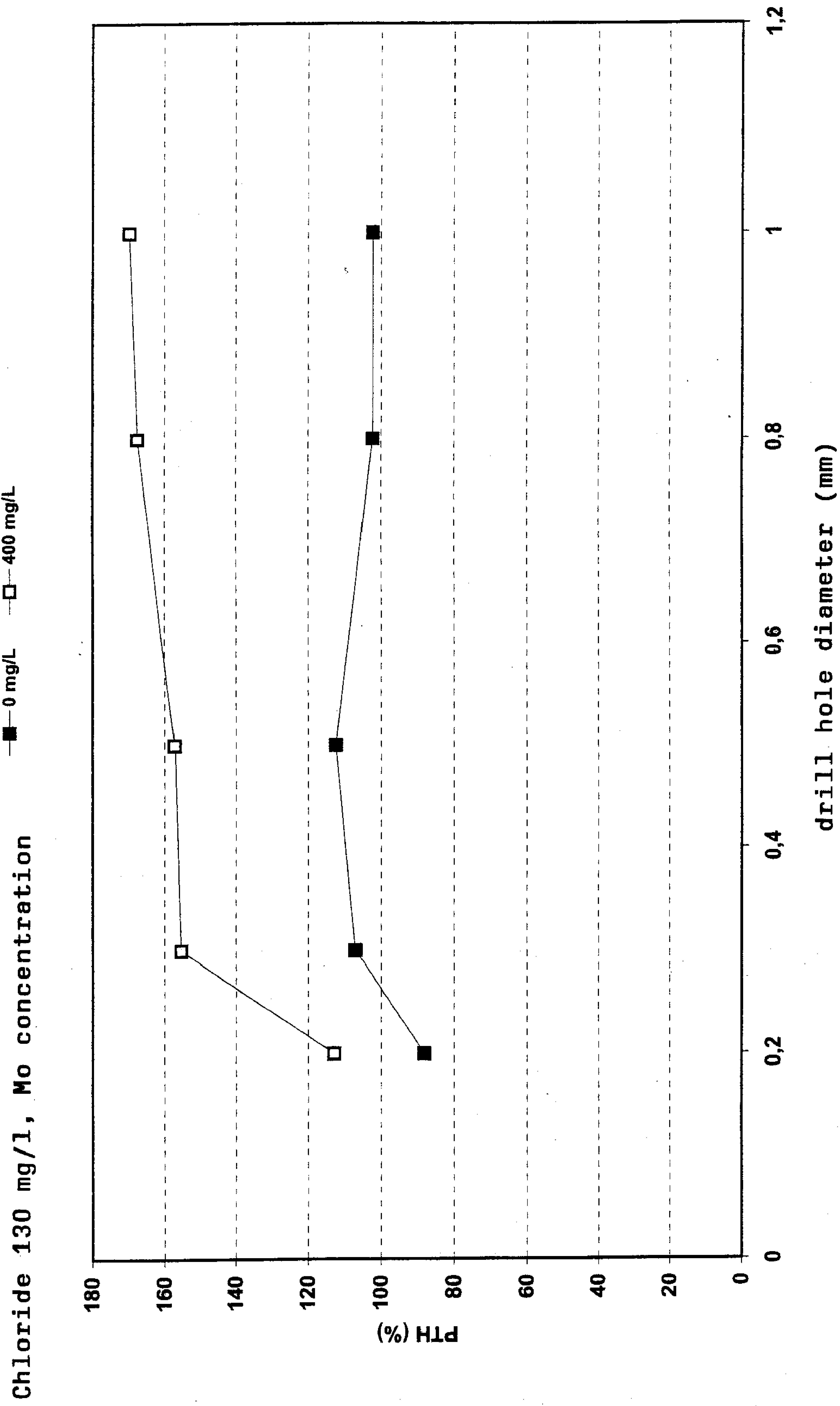


Fig. 2

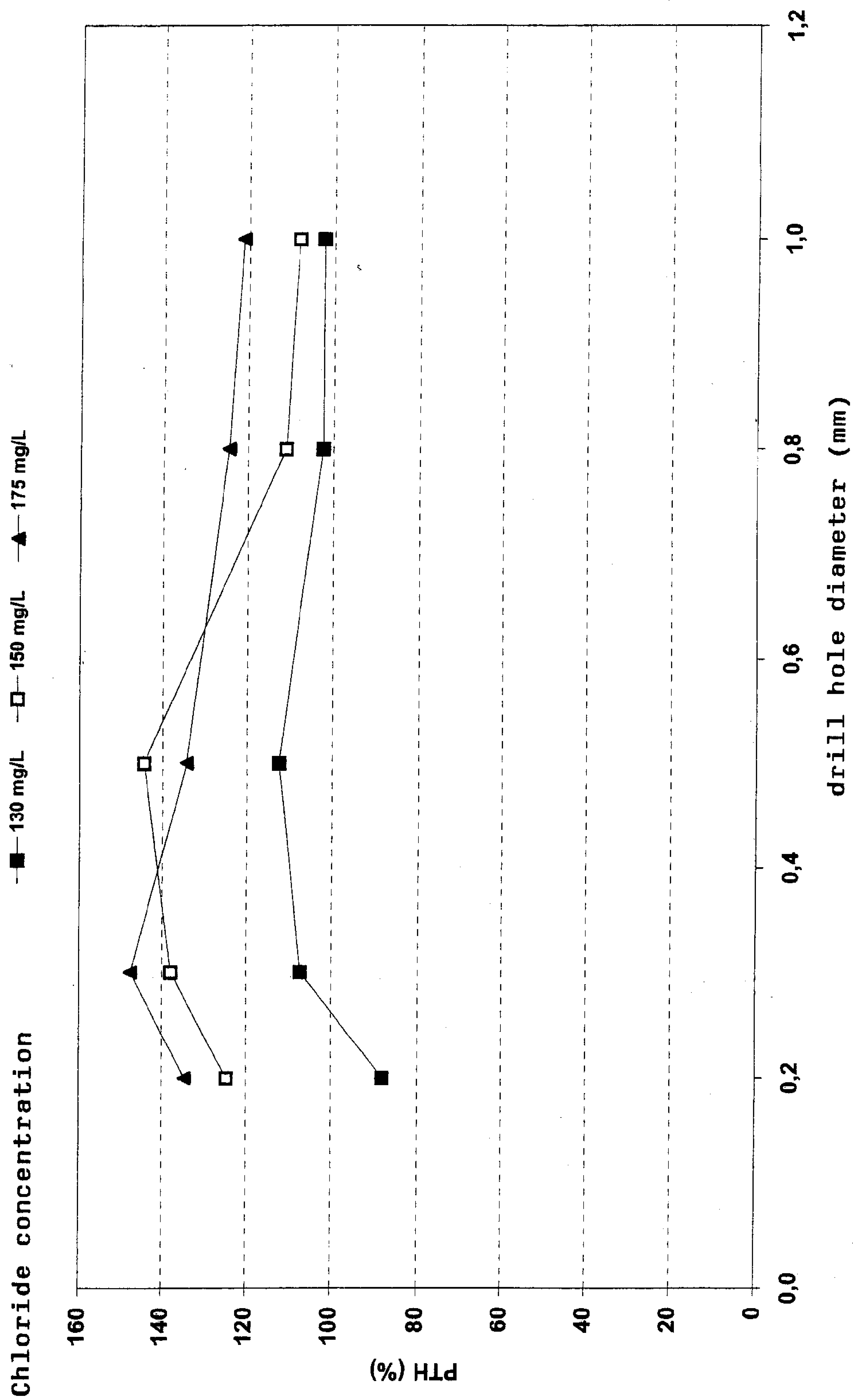


Fig. 3

ELECTROPLATING PROCESS AND COMPOSITION

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority from EP patent application number 05009183.4, the entire disclosure of which is explicitly incorporated by reference.

FIELD OF THE INVENTION

[0002] The invention relates to an electrolytic plating bath for use in decorative, functional, and electronics applications.

BACKGROUND OF THE INVENTION

[0003] Electrolytic plating methods, for example copper-plating, nickel-plating, zincing, or tinning, are carried out by means of soluble or insoluble anodes. When soluble anodes, also known as active anode systems, are used in an electrolytic plating operation, the anode dissolves during plating. The anode comprises a salt of the metal ion being plated. Accordingly, a balance between the dissolution of the soluble anode during plating to yield additional metal ion in the plating composition and metal ion reduction at the cathode allows for careful control of a steady state concentration of metal ion in solution. Insoluble anodes, also referred to as inert anode systems, do not dissolve during the electrolysis because insoluble anodes are constituted of an inert material. Typically, insoluble anodes comprise a carrier material coated with an active layer material. Typical carrier materials, including titanium, niobium, stainless steel, and other inert metals such as valve metals, become passive, i.e., non-corroding, under electrolysis conditions. Typical active layer materials, which are electron-conductive materials, include platinum, iridium, ruthenium, other precious metals, mixed oxides thereof, or compounds of these elements. Herein, the active material can either be directly applied as a layer on the surface of the carrier material, or it can be placed on a substrate which is spaced with respect to the carrier material. Substrate materials include the same types of materials appropriate for use as carrier materials, for example stainless steel, titanium, and the like.

[0004] Generally, electrolytic plating can be carried out by means of direct-current, pulse current, or pulse periodic reverse current.

[0005] Additives including organic additives are typically added to electrolytic plating compositions, which additives act, for example, to brighten the metal deposit, to increase the deposit hardness and/or the dispersion.

[0006] During the electrolytic plating operation, gases, for example oxygen or chlorine, are generated at the insoluble anode. These gases can oxidize organic additives contained in the electrolytic plating bath, which can lead to partial or even complete decomposition of these additives. Decomposition of the organic additives is disadvantageous for at least a couple reasons. First, the additives have to be periodically replenished. Second, degradation products of the additives cause disturbances, such that it becomes necessary to frequently renew or purify or regenerate the electrolytic plating baths, which is economically and ecologically disadvantageous.

[0007] EP 1 102 875 B1 discloses a method for inhibiting organic additive oxidation in an alkaline electrolytic plating bath by separating the anode from the cathode with an ion exchanger membrane. This design has the advantage that organic compounds are isolated from the anode, which effectively prevents oxidation of the additives. However, this design requires more instrumentation, since the electrolytic plating bath requires a closed box with an anodic electrolytic solution around the anode and a cathodic electrolytic solution around the cathode. Additionally, a higher tension is required, which questions the economic efficiency of the design. Importantly, the structural solution proposed by EP 1 102 875 B1 is not applicable to every anode-cathode geometry, such as for coating the interior of tubes.

[0008] DE 102 61 493 A1 discloses an anode comprising an anode base body and a screen for the anode base body. In contrast to the design according to EP 1 102 875 B1, the use of such an anode requires less instrumentation, but only a reduced distribution of layer thicknesses can be obtained in a disadvantageous way on the work piece, i.e. the cathode. Furthermore, despite the screen, gases, such as oxygen, can be generated at the anode, which can lead to an oxidation of organic additives in the electrolytic plating bath. Consequently, the deposition process described in DE 102 61 493 A1 also presents an excessively high consumption of reagents, which requires metrology, i.e., monitoring of and periodic replenishment of bath components and periodic filtering.

[0009] WO 2004/038070 A2 discloses the use of pulse reverse currents for the deposition of copper from acidic copper electrolytic plating baths. The electrolytic plating baths, which are exemplified therein, have a chloride concentration between 10 and 500 mg/L, usually about 80 mg/L.

[0010] U.S. Pat. Pub. No. 2002/0036144 discloses polyvinylpyrrolidone containing copper electrolytic plating compositions for the deposition of copper. The electrolytic plating compositions disclosed therein comprise 70 mg/L HCl, which corresponds to a chloride content of 68 mg/L.

[0011] U.S. Pat. Pub. No. 2003/0851 33 Al discloses electrolytic plating compositions for the galvanic deposition of copper. The compositions can have chloride content between 20 and 200 mg/L.

[0012] U.S. Pat. No. 6,610,192 discloses copper electrolytic plating compositions. The electrolytic compositions described therein can contain 1 to 300 g/L, preferably 150 to 250 g/L of an acid. HCl is disclosed as suitable acid. The chloride content described in the examples is about 50 mg/L.

[0013] U.S. Pat. No. 5,972,192 describes chloride containing copper electrolytic plating compositions for pulse electrolytic plating methods.

SUMMARY OF THE INVENTION

[0014] Based upon the above mentioned state of the art, therefore among the aspects of the invention may be noted the provision of an improved electrolytic plating bath for the use of direct-current, pulse current, or pulse periodic reverse current, which overcomes the disadvantages present in conventional electrolytic plating baths.

[0015] Briefly, therefore, in one aspect the invention is directed to an electrolytic plating composition for electro-

lytically plating a metal onto a substrate comprising a source of deposition metal ions in an amount sufficient to electrolytically deposit the metal onto the substrate, a source of chloride ions in an amount sufficient to provide chloride ions in a concentration of at least 70 mg/L, and a source of a d-block metal ions selected from the group consisting of molybdenum, vanadium, zirconium, tantalum, tungsten, hafnium, and titanium in an amount sufficient to provide between about 5 mg/L and about 5000 mg/L of the d-block metal ions.

[0016] In another aspect the invention is directed to a process for electrolytic plating a metal deposit onto a substrate, the process comprising immersing the substrate into an electrolytic plating bath comprising a cathode, an anode, and an electrolytic plating composition comprising a source of deposition metal ions in an amount sufficient to electrolytically deposit the metal onto the substrate, a source of chloride ions in an amount sufficient to provide at least 70 mg/L chloride ions into the composition, and a source of a d-block metal ions selected from the group consisting of molybdenum, vanadium, zirconium, tantalum, tungsten, hafnium, and titanium in an amount sufficient to provide between about 5 mg/L and about 5000 mg/L of the d-block metal; and supplying electrical current to the electrolytic plating bath to deposit metal onto the substrate.

[0017] Other objects and features will be in part apparent and in part pointed out hereinafter.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] **FIG. 1** is a schematic side view of the multi-phase anode **1** according to the invention. This anode **1** comprises an anode base body **2** and a screen **3**.

[0019] **FIG. 2** is a graph showing the improvement in layer thickness distribution of plated through holes, especially at larger diameter through holes, plated from an acidic copper electrolytic plating composition with added molybdenum (Curve B) compared to a comparable acidic copper electrolytic plating composition without added molybdenum (Curve A). The data used to construct the graph were acquired according to the method of Example 4.

[0020] **FIG. 3** is a graph showing the improvement in layer thickness distribution of plated through holes, especially at smaller diameter through holes, plated from acidic copper electrolytic plating compositions with a low concentration of chloride ion (Curve A), an intermediate concentration of chloride ion (Curve B), and a high concentration of chloride ion (Curve C). The data used to construct the graph were acquired according to the method of Example 5.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0021] The present invention is directed to an electrolytic plating bath for use in decorative, functional, and electronics applications. The applicable substrates include metal substrates and activated plastic substrates requiring a decorative or functional coating, and substrates such as silicon wafers and others for use in the electronics industry. In one aspect the invention is directed to a combination of bath components—d-block metal and elevated Cl content as described below—for which neither the metal being deposited nor the nature of the substrate are critical. In another aspect the invention is directed to this combination in further combination with a specific anode design, and/or in specific metal deposition systems.

[0022] The electrolytic plating composition comprises a source of chloride ions in amount sufficient to provide at least about 70 mg/L chloride and a source of a d-block metal ions selected from the group consisting of molybdenum, vanadium, zirconium, tantalum, tungsten, hafnium, and titanium in an amount sufficient to provide between about 5 mg/L and about 5000 mg/L of the d-block metal, preferably between about 200 mg/L and about 1200 mg/L of the d-block metal. Sources of the chloride ions can include hydrochloric acid, salts, and chloride impurities from low purity copper sources. Sources of the mentioned d-block elements include anions, polyanions of their oxy-acids, cations of their acid anhydrides in highly acid solution, and hetero-polyanions, such as for example as silicometallates.

[0023] The electrolytic plating composition of the present invention can be used in conjunction with a multi-phase anode. Surprisingly, the use of a bi-phase or multi-phase anode in combination with a high chloride concentration, i.e., more than 70 mg/L chloride, leads to excellent coating results. The combination of elements in the electrolytic plating composition of the present invention is particularly suitable for use in a copper electrolytic plating composition because the high chloride content leads to a finer copper crystal structure as well as to a better distribution of the layer thicknesses.

[0024] The advantages obtained by the electrolytic plating bath of the present invention were not expected because the chloride content in electrolytic plating baths using an active electrode system is typically on the order of about 80 mg/L or less. With higher chloride concentration, typically, the soluble copper electrodes become passive. Additionally, if an active electrode system is used, higher chloride content leads to an enrichment of degradation products, such that filtering, for example, with activated carbon, becomes necessary within a short time after initiation of copper plating.

[0025] Moreover, the electrolytic plating baths can be used with higher current densities to yield a faster copper deposition.

[0026] Finally, the source of copper ions can be a cheaper copper oxide source, in which the purity of the copper ion source is not a critical factor. Because of cost differences between pure (i.e., greater than 99% purity) copper ion sources and less pure (less than 90%, 80%, or even less than 70% purity) copper ion sources, the use of the electrolytic plating bath of the present invention results in substantial cost savings.

[0027] With regard to the multi-phase anode, the term "multi-phase" is meant to describe an anode comprising a base body and one screen or more than screen. The simplest anode configuration, in which the anode comprises a base body and one screen can be referred to as a "bi-phase" anode. Accordingly, the anode base body is the first phase, and the screen is the second phase. An anode configuration in which the anode comprises a base body and two screens can be referred to as a "tri-phase" anode. The anode base body itself comprises a carrier material and an active material. The carrier material can be valve metals such as titanium, niobium, zirconium, hafnium, lanthanum, tanta-

lum, and tungsten, and alloys thereof and ferrous metal alloys such as, for example, steel and stainless steel alloys including nickel plated steel and nickel/cobalt plated steel, and nickel and nickel-based alloys such as the Hastelloy alloys. The Hastelloy alloys are available from Haynes International, Inc. (Kokomo, Ind.) and are nickel-based alloys comprising molybdenum, chromium, and cobalt as major components in varying proportions. Typically, the carrier materials can be shaped as plates, rods, tubes, and in a basket configuration. Plates are typically about 10 cm to about 20 cm in width, about 2 mm thick, and about 1 m to about 1.5 m in length. Rods are typically about 10 mm to about 20 mm in diameter and about 1 m to about 1.5 m in length. Tubes are typically about 5 cm to about 10 cm in diameter and about 1 m to 1.5 m in length, which are closed at the end which is exposed to the metal plating baths.

[0028] The active material can be applied as a layer directly onto the carrier metal, or can be a spaced apart from the carrier metal (for example, on a substrate spaced apart from the carrier metal). In the preferred embodiment, it is a precious metal-based active material. Active materials include iridium, platinum, ruthenium, other precious metals, compounds thereof, and in particular the mixed oxides thereof are suitable. An exemplary mixed oxide comprises about 41 wt. % oxygen, about 39 wt. % ruthenium, and about 20 wt. % iridium.

[0029] The screen of the anode can be disposed around the anode in a manner in which the screen is in direct contact with the anode base body and forms a bag which envelopes the anode base body, or the screen can envelope the anode base body in a manner which minimally separates the screen from direct contact with the anode base body. Accordingly, the screen is disposed in such a manner in which the screen is wrapped around the base body, or in a manner in which the distance between the screen and the base body is less than about 5 mm, preferably between about 2 mm and about 0.5 mm. The screen can be composed of non-conductive material, such as plastic or glass, or a self-passivating metal (i.e., does not flow a current) such as titanium. The screen can be a fabric, a net, or a grid. The screen can be single or multi-layered. These terms used to describe the types of screens differentiate the screens with respect to their flexibility. That is, a fabric is a flexible screen such as a semi-permeable membrane, while a grid, which is a woven, expanded metal, is the most rigid. A net has flexibility intermediate that of a fabric or a grid.

[0030] In one embodiment, the screen comprises a grid or net made of self-passivating metal (i.e., does not flow a current) such as titanium or valve metals. Exemplary valve metals include niobium, zirconium, hafnium, lanthanum, tantalum, and tungsten, and alloys thereof. The grid acts as a physical barrier which prevents oxygen bubbles from entering into the bulk of the electrolytic plating composition and allows the bubbles to migrate to the surface behind the grid. This is advantageous because it decreases the oxidation of bulk additives. A plastic grid can act in the same manner, but a titanium grid is preferred because titanium acts as an additional electrochemical element which results in reduced oxidation of bulk additives. The grid or net can have a mesh size between about 0.5 and about 1 mm.

[0031] In one embodiment, the screen is formed by a fabric made of non-conductive material such as organic materials or inorganic, non-metallic materials. Exemplary organic materials include polypropylene, polyethylene, polyvinylchloride (PVC), chlorinated PVC, PC, cotton fibers, or linens. Exemplary inorganic, non-metallic materials include glass fibers and mineral fibers, such as fiberglass, glass wool, glass filament, and refractory ceramic fibers (RCF). The fabric can be formed into a porous diaphragm, such as a bag which surrounds and envelopes the anode base body. The fabric comprises an interwoven network of fibers, the fibers woven horizontally and vertically. The fabric materials can include polypropylene fibers, glass fibers, and mineral fibers. Accordingly, the diameter of the fibers is typically between about 0.1 mm and about 0.5 mm, and the porous spaces between the fibers are typically no more than about 0.5 mm. In embodiments where the anode is shaped like a rod or tube, preferably, the anode screen comprises a fabric, wrapped like a sock, around the anode base body. An exemplary fabric is available from Fritsche GmbH & Co., which is constructed from polypropylene (235 g/m^2 weight, 0.75 mm thickness, 50 to 60 L/min air permeability, and tensile strength of 1400 N/5 cm warp and 1200 N/5 cm weft).

[0032] Preferably, the multi-phase anode comprises a two-part screen, wherein the first part of the screen is a fabric made of polypropylene and the second part of the screen is formed by a grid or network made of titanium. This particular two-part screen is preferred for a flat anode. The titanium has in connection with the anode a positive potential, but because of its self-passivating properties does not flow a current. The positive potential reduces the diffusion/migration of positive charged ions to the anode surface, which yields better results. In the preferred embodiment, the fabric made of polypropylene is placed between the anode body and the grid or network made of titanium. Accordingly, the anode is a tri-phase anode.

[0033] The bi-phase or multi-phase electrode system inhibits contamination of the electrolytic plating composition with oxygen by blocking the diffusion of oxygen into the bulk of the electrolytic plating composition. Rather, the oxygen is retained by the screen or screens surrounding the anode base body. Oxygen present in excess of its solubility limit in water diffuses to the surface of the electrolytic composition rather than oxidizing organic additives and degrading the bath quality. Accordingly, the screen/fabric system is open at the surface of the bath to permit gas to escape.

[0034] The electrolytic plating bath according to the invention thus proves to be especially economic. The oxidation of organic additives is substantially reduced because the oxygen concentration in the electrolytic plating composition is controlled. This allows for considerable delay of purification of the electrolytic plating composition, for example by means of activated carbon treatment or classic oxidative treatment. Laboratory investigations, which have been carried out in this context, show that the operating time of the electrolytic plating bath according to the invention can be increased by 300% or more in comparison to electrolytic plating baths known in the art.

[0035] **FIG. 1** depicts an exemplary multi-phase anode, depicted generally by the number 1. The anode base body **2** comprises a carrier material **4** and an active material **5**. Carrier material **4** is preferably stainless steel, titanium or

the like, whereas the active material **5** is preferably made of iridium mixed oxide, platinum, ruthenium, or another precious metal. The active material **5** can either be directly applied on said carrier material **4** or be spaced from the carrier material **4**. In the exemplary embodiment according to **FIG. 1**, the active material **5** is spaced from said carrier material **4**, wherein the distance between carrier material **4** and active material **5** is referenced by A. This distance A can be for example some tenths of a millimeter. In the exemplary embodiment according to **FIG. 1**, active material **5** is carried by a substrate, which can be composed of stainless steel, titanium or the like.

[0036] The screen **3** of anode **1** is a two-part screen, as shown in **FIG. 1**. A first part of said screen **3** is formed by a fabric **6** composed of a non-conductive material, such as plastic (e.g. polypropylene), glass fiber or mineral fiber, or by porous, non-conductive diaphragms. The second part of screen **3** consists of a grid or network **7** made of titanium. Said screen **3** is spaced from the anode base body **2**, wherein the distance B between said anode base body **2** and the polypropylene fabric can be between about 0.01 and about 10 mm. The second part of said screen **3**, i.e., the grid or network **7** made of titanium, is also spaced from the first part of screen **3**, i.e. fabric **6** made of polypropylene, wherein the distance C can also be between about 0.1 mm and about 10 mm. Other dimensions are also possible, dependent on the tank configuration and the application field of the electrolytic plating bath.

[0037] Accordingly, the above mentioned distance indications are not to be considered as limiting for the invention. The following list of reference numbers is provided for convenience:

[0038] anode

[0039] anode base body

[0040] screen

[0041] carrier material

[0042] coating

[0043] fabric

[0044] grid or network

[0045] A. space between carrier and anode base body

[0046] B. space between active layer and interior screen

[0047] C. space between interior screen and exterior screen

[0048] As explained above, the electrolytic plating bath of the present invention comprises an electrolytic plating composition comprising a relatively high concentration of chloride and a source of d-block metals, the d-block metals selected from the group consisting of molybdenum, vanadium, zirconium, tantalum, tungsten, hafnium, and titanium.

[0049] Some of the disadvantages known in the art with respect to high chloride content, i.e., passivation of the soluble copper anode and enrichment of degradation products, are overcome by the use of a multi-phase, inert electrode system. Accordingly, the electrolytic plating composition comprises a source of chloride ions sufficient to yield a concentration of chloride ions of at least about 70 mg/L, such as at least about 90 mg/L, preferably between about 90 mg/L and about 5000 mg/L, more preferably between about 100 mg/L and about 300 mg/L, even more preferably between about 120 mg/L and about 250 mg/L. Sources of chloride ions include alkali metal chlorides, such as sodium chloride (NaCl), chloride-containing acids such as hydrochloric acid (HCl), and when the electrolytic plating bath is a copper electrolytic plating bath, copper chlorides and even low purity copper oxides which have chloride ion impurity. The inventors have discovered that the upper concentration of chloride ion is not narrowly critical such that the chloride impurity concentration from the copper source does not adversely affect the quality of the deposit or the stability of the electrolytic plating bath.

[0050] Accordingly, cost savings are an important advantage of the present invention. A cheap, relatively impure copper source can be used as a soluble anode. If an inert anode is used, copper oxide or another copper compound, i.e., copper chloride, can be used for the regeneration of the depleted copper. The price of the used copper oxide is proportional to the impurity, such as chloride, content. Highly pure copper ion sources, such as copper oxide, containing very little chloride impurity, can be expensive. The present invention, because high chloride concentrations are not detrimental to the plating bath's efficacy, allows the use of impure, high chloride content copper ion sources, which permits the use of especially cheap copper oxide for regeneration purposes.

[0051] Moreover, it has been discovered that the high chloride content advantageously plates a copper deposit having a finer crystal structure. Without being bound to a particular theory, it is thought that the chloride enhances the formation of slightly soluble copper(I) chloride precipitates over the active sites of copper deposition. Active sites are regions of high current density. These precipitates effectively temporarily poison the active sites against additional copper deposition. Accordingly, current density flows from these poisoned active sites to regions of low current density causing copper ions migration to these areas and causing the growing copper deposit to form new nucleates for additional copper deposition. The competition between copper(I) chloride precipitates and copper ions at the active sites of the copper deposits results in a more level deposit comprised of finer, smaller copper crystals. Additionally, where pulse periodic reverse current is used, the chloride improves throwing power because the copper(I) chloride precipitates increase the amount of copper(I) available for plating after the reverse current phase.

[0052] The electrolytic plating composition of the present invention further comprises a source of d-block elements, the d-block elements selected from the group consisting of molybdenum, vanadium, zirconium, tantalum, tungsten, hafnium and titanium. The sources of these d-block elements include anions or polyanions of their oxyacids, in highly acid solution also in form of cations of their acid anhydrides or also as hetero-polyanions, such as for example as silicometallates. The sources of the d-block metals are added in an amount sufficient to provide between about 5 mg/L and about 5000 mg/L of the d-block metal, preferably between about 200 mg/L and about 1200 mg/L of the d-block metal. The addition of these materials leads to a further improvement of the crystallinity (grain refiner) and distribution of the layer thicknesses.

[0053] Exemplary sources of molybdenum oxides include molybdic acids; molybdic acid salts of ammonium, tetramethylammonium, and alkali metals; heteropoly acids of molybdenum; and other mixtures thereof. Molybdenum oxides species include molybdenum salts such as MoO_3 predissolved with TMAH; $(NH_4)_2MoO_4$; Na_2MoO_4; $Na_2MoO_4.2H_2O$; $(NH_4)_6Mo_7O_{24}.4H_2O$; $(NH_4)_6Mo_8O_{27}.4H_2O$; dimolybdates ($Me_2Mo_2O_7.nH_2O$) such as $(NH_4)_2Mo_2O_7.nH_2O$; trimolybdates ($Me_2Mo_3O_{10}.nH_2O$) such as $(NH_4)_2Mo_3O_{10}.2H_2O$; tetramolybdates ($Me_2Mo_4O_{13}$); metamolybdates ($Me_2H_{10-m}[H_2(Mo_2O_7)_6].nH_2O$; wherein m is less than 10); hexamolybdates ($Me_2Mo_6O_{19}.nH_2O$); octamolybdates ($Me_2Mo_8O_{25}.nH_2O$); paramolybdates ($Me_2Mo_7O_{22}.nH_2O$ and $Me_{10}Mo_{12}O_{41}.nH_2O$). In the above, Me is a counterion selected from among ammonium, tetramethylammonium, and alkali metal cations, and n is an integer having a value corresponding to a stable or metastable form of the hydrated oxide.

[0054] Exemplary sources of vanadium include vanadate salts such as triammonium salts, metavanadate salts such as ammonium or sodium salts, pyrovanadates ($V_2O_7^{4-}$), hexavanadates ($HV_6O_{17}^{3-}$), V_2O_3, V_2O_4, V_2O_5, vanadium silicometallates, and vanadium silicofluorides.

[0055] Exemplary sources of zirconium include water soluble zirconium compounds, such as zirconate salts (ZrO_3^{2-}) of ammonium, alkali metals, and alkaline earth metals, zirconium oxides (ZrO_2) and silicates, and zirconium chloride reacted with water.

[0056] Exemplary sources of tantalum include water soluble tantalum compounds such as tantalum oxide (Ta_2O_5), and tantalum chloride ($TaCl_5$).

[0057] Exemplary sources of W ions are tungsten trioxide, tungstic acids, ammonium tungstic acid salts, tetramethylammonium tungstic acid salts, and alkali metal tungstic acid salts, phosphotungstic acid, silicotungstate, other heteropolytungstic acids, and combinations thereof.

[0058] Exemplary sources of hafnium include water soluble hafnium compounds such as hafnium oxide (HfO_2), hafnium chloride ($HfCl_4$), and hafnium oxychloride hydrates ($HfOCl_2.xH_2O$)

[0059] Exemplary sources of titanium include water soluble titanium compounds such as titanium oxides, titanium oxide salts (TiO_3^{2-}) of ammonium and metals, and titanium chloride ($TiCl_2$).

[0060] Especially preferred sources of d-block metals are sources of molybdenum, such as, for example, sodium molybdate. Using a direct current, added molybdenum acts as a grain refiner. Using pulse periodic reverse current, added molybdenum acts as grain refiner but additionally increases the throwing power of the electrolytic plating composition, especially when plating low aspect ratio (i.e., large diameter) through holes. When the electrolytic plating composition comprises added molybdenum and a high chloride ion concentration, the use of pulse periodic reverse current increases the throwing power of the electrolytic plating composition at both low aspect ratio and high aspect ratio (i.e., small diameter) through holes. Accordingly, a preferred embodiment of the electrolytic plating composition comprises both a source of molybdenum and a high concentration of chloride ion.

[0061] The components of the electrolytic plating composition may vary widely depending on the substrate to be plated and the type of metal deposit desired.

[0062] In those embodiments where copper is the metal to be plated, the electrolytic plating baths can be acidic or alkaline. A variety of Cu electrolytic plating baths are described in the book entitled Modern Electroplating, edited by F. A. Lowenheim, John Reily & Sons, Inc., 1974, pages 183-203. Exemplary Cu electrolytic plating baths include Cu fluoroborate, Cu pyrophosphate, Cu cyanide, Cu phosphonate, and other Cu metal complexes such as methane sulfonic acid. The most typical Cu electrolytic plating bath comprises Cu sulfate in an acid solution.

[0063] The concentration of Cu and acid may vary over wide limits; for example, from about 4 to about 70 g/L Cu and from about 2 to about 240 g/L acid. In this regard the compounds of the invention are suitable for use in distinct acid/Cu concentration ranges, such as high acid/low Cu systems, in low acid/high Cu systems, and mid acid/high Cu systems. In high acid/low Cu systems, the Cu ion concentration can be on the order of 4 g/L to on the order of 30 g/L; and the acid concentration may be sulfuric acid in an amount of greater than about 100 g/L up to about 240 g/L. In one high acid/low Cu system, the Cu ion concentration is about 25 g/L where the H_2SO_4 concentration can be between about 180 g/L and about 240 g/L. In some low acid/high Cu systems, the Cu ion concentration can be between about 35 g/L and about 60 g/L, such as between about 38 g/L and about 42 g/L. In some low acid/high Cu systems, the Cu ion concentration can be between about 46 g/L and about 60 g/L, such as between about 48 g/L and about 52 g/L. (35 g/L Cu ion corresponds to about 140 g/L $CuSO_4.5H_2O$ Cu sulfate pentahydrate.) The acid concentration in these systems is preferably less than about 100 g/L. In some low acid/high Cu systems, the acid concentration can be between about 5 g/L and about 30 g/L, such as between about 10 g/L and about 15 g/L. In some low acid/high Cu, the acid concentration can be between about 50 g/L and about 100 g/L, such as between about 75 g/L to about 85 g/L. In an exemplary low acid/high Cu system, the Cu ion concentration is about 40 g/L and the H_2SO_4 concentration is about 10 g/L. In another exemplary low acid/high Cu system, the Cu ion concentration is about 50 g/L and the H_2SO_4 concentration is about 80 g/L. In mid acid/high Cu systems, the Cu ion concentration can be on the order of 30 g/L to on the order of 60 g/L; and the acid concentration may be sulfuric acid in an amount of greater than about 50 g/L up to about 100 g/L. In one mid acid/high Cu system, the Cu ion concentration is about 50 g/L where the H_2SO_4 concentration is about 80 g/L.

[0064] Exemplary copper ion sources include copper sulfate, copper sulfate pentahydrate, copper chloride, and copper oxides. Especially preferred copper ion sources in the context of this invention are low purity copper oxides, both because they are much cheaper than high purity sources and because they add additional chloride ion impurity into the electrolytic plating baths, which chloride ion acts, as described above, to level the deposit and grow finer crystals.

[0065] Additives are used in the bath to provide desired surface finishes for the plated metal and other deposition characteristics. Usually more than one additive is used with each additive forming a desired function. An activator (also referred to as an accelerator) and suppressor are preferably

used for improved metal physical (such as brightness), structural, and electrical properties (such as electrical conductivity and reliability). Particular additives (usually organic additives) are used for grain refinement, suppression of dendritic growth, and improved covering and throwing power. Typical additives used in electrolytic plating are discussed in a number of references including Modern Electroplating, cited above.

[0066] With regard to activators, in a system currently preferred by the applicants, the activator is from about 0.2 to about 1.2 ml/L of a bath soluble organic divalent sulfur compounds as disclosed in U.S. Pat. No. 6,776,893, the entire disclosure of which is expressly incorporated by reference. The preferred suppressor is from about 0.8 to about 1.5 ml/L of a bath soluble polyether compound as also disclosed in U.S. Pat. No. 6,776,893.

[0067] The invention further proposes a method for electrolytic plating, in which an electrolytic plating bath presenting the above mentioned characteristics is used. Substrates applicable for plating with the compositions of the present invention include semiconductor integrated circuit devices having high aspect ratio features such as vias and trenches and printed circuit boards having lower aspect ratio features and drilled through holes.

[0068] Plating equipment for plating substrates is well known and is described in, for example, Haydu et al., U.S. Pat. No. 6,024,856. Plating equipment comprises an electrolytic plating tank which holds the copper electrolytic plating composition and which is made of a suitable material such as plastic or other material inert to the electrolytic plating composition. The tank may be cylindrical, especially for wafer plating. A cathode is horizontally or vertically disposed at the upper part of the tank and may be any type substrate such as decorative component, a functional component, or a silicon wafer having openings such as trenches and vias or printed circuit boards having drill holes. Wafer substrates are typically coated first with a barrier layer, which may be titanium nitride, tantalum, tantalum nitride, or ruthenium to inhibit Cu diffusion and next with a seed layer of Cu or other metal to initiate Cu superfilling plating thereon. A Cu seed layer may be applied by chemical vapor deposition (CVD), physical vapor deposition (PVD), or the like. The multi-phase anode is horizontally disposed at the lower part of tank forming a space between the anode and cathode.

[0069] The cathode substrate and anode are electrically connected by wiring and, respectively, to a rectifier (power supply). The cathode substrate for direct or pulse current has a net negative charge so that Cu ions in the solution are reduced at the cathode substrate forming plated Cu metal on the cathode surface. An oxidation reaction takes place at the anode. The cathode and anode may be horizontally or vertically disposed in the tank.

[0070] During operation of the electrolytic plating system, Cu metal is plated on the surface of a cathode substrate when the rectifier is energized. A pulse current, direct current, pulse periodic reverse current, or other suitable current may be employed. In a preferred embodiment, plating is carried out by means of pulse periodic reverse current, especially where the electrolytic plating composition comprises both a source of molybdenum and a high chloride ion concentration. The temperature of the electrolytic solution may be maintained using a heater/cooler whereby electrolytic solution is removed from the holding tank and flows through the heater/cooler and then is recycled to the holding tank.

[0071] Electrolysis conditions such as electric current concentration, applied voltage, electric current density, and electrolytic solution temperature are essentially the same as those in conventional electrolytic Cu plating methods. For example, the bath temperature is typically about room temperature such as about 20-27° C., but may be at elevated temperatures up to about 40° C. or higher. In direct current plating, the electrical current density is typically up to about 100 mA/cm^2, typically about 2 mA/cm^2 to about 60 mA/cm^2. It is preferred to use an anode to cathode ratio of about 1:1, such as about 0.8:1 to about 1:1, but this may also vary widely from about 1:4 to 4:1. The process also uses mixing in the electrolytic plating tank which may be supplied by agitation or preferably by the circulating flow of recycle electrolytic solution through the tank. The flow through the electrolytic plating tank provides a typical residence time of electrolytic solution in the tank of less than about 1 minute, more typically less than 30 seconds, e.g., 10-20 seconds.

[0072] By using the electrolytic plating bath according to the methods described herein, a fine crystal structure can be obtained, which leads to improved physical properties of the deposited layer.

[0073] The following examples further illustrate the present invention.

EXAMPLE 1

Acidic Copper Electrolytic Plating Composition of the Present Invention

[0074] An acidic copper electrolytic plating composition was prepared having the following components:

[0075] i. 175 mg/L chloride ion (from sodium chloride)

[0076] ii. 400 mg/L molybdenum ion (from sodium molybdate)

[0077] iii. 180 to 240 g/L sulfuric acid

[0078] iv. 100 g/L copper sulfate pentahydrate

[0079] v. 0.5 ml/L activator

[0080] vi. 0.8 ml/L suppressor

[0081] This electrolytic plating composition was prepared, having the concentrations above on a per Liter basis, according to the following protocol:

[0082] Add a sufficient amount of sulfuric acid to yield desired concentration to deionized water (60% of final solution volume).

[0083] Dissolve a sufficient amount of copper sulfate pentahydrate to yield desired concentration in the sulfuric acid solution.

[0084] Add deionized water to the desired solution volume.

[0085] Dissolve a sufficient amount of sodium chloride to yield desired chloride ion concentration to copper solution.

[0086] Dissolve sufficient amounts of activator and suppressor to yield desired concentrations of each in the copper electrolytic plating composition.

EXAMPLE 2

Electrolytic Plating Using an Acidic Copper Electrolytic Plating Composition of the Present Invention

[0087] An anode was employed comprising titanium carrier, a mixed oxide of iridium and ruthenium active layer, a polypropylene fabric, and a titanium screen according to the configuration described above and illustrated in **FIG. 1**. The electrolytic plating bath employing the composition described in Example 1 was used to plate through holes and vias in a Printed Circuit Board substrate. For comparison, an electrolytic plating bath employing the composition described in Example 1 was used to plate similar substrates using a conventional insoluble anode consisting of mixed oxides of Ir and Ru. Plating was carried out with each bath for 60 min.

[0088] The consumption of bath additives was measured by measuring the consumption rate of the added activator. Using the conventional insoluble anode consisting of mixed oxides of Ir and Ru, the consumption of the activator was determined to be approximately 550 mL per kAh. By comparison, the consumption of the activator using the anode comprising titanium carrier, a mixed oxide of iridium and ruthenium active layer, and a titanium grid was determined to be approximately 250 mL per kAh. Accordingly, the activator consumption rate was decreased by more than 50% using the multi-phase anode of the invention. Additional tests showed the activator consumption with the inert anode with the Ti-grid to be about 250 ml/kAh, and with the anode bag to be less than 200 ml/kAh.

EXAMPLE 3

Layer Thickness Distribution

[0089] Six acidic copper electrolytic plating compositions were prepared each comprising copper sulfate pentahydrate (100 g/L), sulfuric acid (180 to 240 g/L), activator, and suppressor. The chloride concentration was varied, as shown in the following table:

Bath No.	Chloride Concentration (mg/L)	Layer thickness distribution (dispersion)
1	75	75%
2	100	89%
3	125	102%
4	150	125%
5	175	132%
6	250	99%

[0090] The layer thickness distribution measures the difference in height of the plated copper at the center of the hole compared to the edges of the plated through hole. For this example, the average layer thickness distribution of 10 holes having different diameters and aspect ratios (aspect ratios varied from 1:1 to 10:1) in a printed circuit board results were plated under the following conditions:

[0091] Pulse Periodic Reverse Current

[0092] Ratio of cathodic current density to anodic current density=1:3

[0093] Cathodic current density: 3 ASD

[0094] Ratio of cathodic time to anodic time: 20:1

[0095] Cathodic time: 10 ms.

[0096] Based on the chloride content, different distributions of layer thicknesses can be obtained, which are better than the distributions of layer thicknesses achievable from conventional electrolytic plating baths.

EXAMPLE 4

Current Distribution from Acidic Copper Electrolytic Plating Composition Containing Molybdenum

[0097] Two acidic copper electrolytic plating compositions were prepared.

[0098] Composition A comprised:

[0099] Copper sulfate pentahydrate (100 g/L)

[0100] Sulfuric acid (180 to 240 g/L)

[0101] Chloride ion (130 mg/L)

[0102] Activator (0.5 ml/L)

[0103] Suppressor (1.2 ml/L)

[0104] Composition B comprised:

[0105] Copper sulfate pentahydrate (100 g/L)

[0106] Sulfuric acid (180 to 240 g/L)

[0107] Chloride ion (130 mg/L)

[0108] Activator (0.5 ml/L)

[0109] Suppressor (1.2 ml/L)

[0110] Molybdenum (400 mg/L, from sodium molybdate).

[0111] Compositions A and B were used to plate substrates having through holes of various diameters and aspect ratios. Plating occurred for 60 minutes at room temperature and with agitation. The throwing power of each bath was measured, and the results are shown in **FIG. 2**. It can be seen from **FIG. 2**, that plating with Composition B (Curve B) with added molybdenum exhibited increased throwing power, especially in the large diameter holes, compared with plating with Composition A (Curve A) with no added molybdenum.

EXAMPLE 5

Current Distribution from Acidic Copper Electrolytic Plating Composition Containing Chloride

[0112] Three acidic copper electrolytic plating compositions were prepared.

[0113] Composition A comprised:

[0114] Copper sulfate pentahydrate (100 g/L)

[0115] Sulfuric acid (180 to 240 g/L)

[0116] Chloride ion (130 mg/L)

[0117] Activator (0.5 ml/L)

[0118] Suppressor (1.2 ml/L)

[0119] Composition B comprised:

[0120] Copper sulfate pentahydrate (100 g/L)

[0121] Sulfuric acid (180 to 240 g/L)

[0122] Chloride ion (150 mg/L)

[0123] Activator (0.5 ml/L)

[0124] Suppressor (1.2 ml/L)

[0125] Composition C comprised:

[0126] Copper sulfate pentahydrate (100 g/L)

[0127] Sulfuric acid (180 to 240 g/L)

[0128] Chloride ion (175 mg/L)

[0129] Activator (0.5 ml/L)

[0130] Suppressor (1.2 ml/L)

[0131] Compositions A, B, and C were used to plate substrates having through holes of various diameters and aspect ratios. Plating occurred for 60 minutes at room temperature and with agitation. The throwing power of each bath was measured, and the results are shown in **FIG. 3**. In **FIG. 3**, curve A exhibits the throwing power of Composition A, curve B exhibits the throwing power of Composition B, and curve C exhibits the throwing power of Composition C. It can be seen from **FIG. 3** that as the chloride ion concentration increases, the throwing power of the plating bath increased, especially at smaller diameter holes.

[0132] As the above Examples 4 and 5 show, significantly improved layer thickness distributions can be obtained in both small and large diameter holes by adding chloride ion (which improves throwing power in small diameter holes) and molybdenum (which improves throwing power in large diameter holes).

[0133] In view of the above, it will be seen that the several objects of the invention are achieved and other advantageous results attained.

[0134] When introducing elements of the present invention or the preferred embodiment(s) thereof, the articles "a,""an,""the," and "said" are intended to mean that there are one or more of the elements. The terms "comprising,""including," and "having" are intended to be inclusive and mean that there may be additional elements other than the listed elements.

[0135] As various changes could be made in the above methods and products without departing from the scope of the invention, it is intended that all matter contained in the above description and shown in any accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. An electrolytic plating composition for electrolytically plating a metal onto a substrate, the composition comprising:

a source of deposition metal ions in an amount sufficient to electrolytically deposit the metal onto the substrate;

a source of chloride ions in an amount sufficient to provide chloride ions in a concentration of at least 70 mg/L;

and a source of d-block metal ions selected from the group consisting of molybdenum, vanadium, zirconium, tantalum, tungsten, hafnium, and titanium in an amount sufficient to provide between about 5 mg/L and about 5000 mg/L of the d-block metal ions.

2. The composition of claim 1 wherein the amount of the source of the d-block metal ion is sufficient to provide between about 200 mg/L and 1200 mg/L of the d-block metal ions.

3. The composition of claim 1 wherein the amount of the source of chloride ions is sufficient to provide between about 90 mg/L and about 5000 mg/L chloride ions.

4. The composition of claim 1 wherein the amount of the source of chloride ions is sufficient to provide between about 100 mg/L and about 300 mg/L chloride ions.

5. The composition of claim 1 wherein the amount of the source of chloride ions is sufficient to provide between about 120 mg/L and about 250 mg/L chloride ions.

6. The composition of claim 1 wherein the composition is for Cu plating under acidic conditions and the source of deposition metal ions is a source of Cu ions which provides a Cu ion concentration in the range of about 4 to about 70 g/L.

7. The composition of claim 1 wherein the composition is for Cu plating under acidic conditions and the source of deposition metal ions is a source of Cu ions which provides a Cu ion concentration in the range of about 4 to about 30 g/L.

8. The composition of claim 1 wherein the composition is for Cu plating under acidic conditions and the source of deposition metal ions is a source of Cu ions which provides a Cu ion concentration in the range of about 35 to about 60 g/L.

9. The composition of claim 1 wherein:

the composition is for Cu plating under acidic conditions;

the source of deposition metal ions is a source of Cu ions which provides a Cu ion concentration in the range of about 4 to about 70 g/L;

the source of the d-block metal ion is sufficient to provide between about 200 mg/L and 1200 mg/L of the d-block metal ions; and

the source of chloride ions is sufficient to provide between about 100 mg/L and about 300 mg/L chloride ions.

10. The composition of claim 1 wherein:

the composition is for Cu plating under acidic conditions;

the source of deposition metal ions is a source of Cu ions which provides a Cu ion concentration in the range of about 4 to about 70 g/L;

the source of the d-block metal ion is a source of molybdenum ion sufficient to provide between about 200 mg/L and 1200 mg/L of molybdenum ions as the d-block metal ions; and

the source of chloride ions is sufficient to provide between about 100 mg/L and about 300 mg/L chloride ions.

11. The composition of claim 1 wherein:

the composition is for Cu plating under acidic conditions;

the source of deposition metal ions is a source of Cu sulfate pentahydrate to provide a Cu ion concentration in the range of about 4 to about 70 g/L;

the source of the d-block metal ion is sodium molybdate to provide between about 200 mg/L and 1200 mg/L of molybdenum ions as the d-block metal ions; and

the source of chloride ions is sufficient to provide between about 100 mg/L and about 300 mg/L chloride ions.

12. A process for electrolytic plating a metal deposit onto a substrate, the process comprising:

immersing the substrate into an electrolytic plating bath comprising:

a cathode;

an anode; and

an electrolytic plating composition comprising a source of deposition metal ions in an amount sufficient to electrolytically deposit the metal onto the substrate, a source of chloride ions in an amount sufficient to provide at least 70 mg/L chloride ions into the composition, and a source of a d-block metal ions selected from the group consisting of molybdenum, vanadium, zirconium, tantalum, tungsten, hafnium, and titanium in an amount sufficient to provide between about 5 mg/L and about 5000 mg/L of the d-block metal; and

supplying electrical current to the electrolytic plating bath to deposit metal onto the substrate.

13. The process of claim 12 wherein the electrolytic plating composition is an acid Cu plating composition and the anode comprises an anode base body comprising a carrier material and a precious metal-based active material.

14. The process of claim 12 wherein the electrolytic plating composition is an acid Cu plating composition and the anode comprises an anode base body comprising a carrier material and an active material selected from the group consisting of platinum, iridium, ruthenium, other precious metals, mixed oxides thereof, and compounds thereof.

15. The process of claim 13 wherein the carrier material is a material is selected from the group consisting of titanium, niobium, zirconium, hafnium, lanthanum, tantalum, tungsten, nickel, alloys of the foregoing, stainless steel alloys, nickel-plated steel, and nickel/cobalt plated steel.

16. The process of claim 14 wherein the carrier material is a material is selected from the group consisting of titanium, niobium, zirconium, hafnium, lanthanum, tantalum, tungsten, nickel, alloys of the foregoing, stainless steel alloys, nickel-plated steel, and nickel/cobalt plated steel.

17. The process of claim 12 wherein the anode comprises a screen and an anode base body.

18. The process of claim 12 wherein the anode comprises a screen and an anode base body comprising a carrier metal and a precious metal-based active material.

19. The process of claim 12 wherein the anode comprises a screen disposed around an anode base body with spacing between the screen and the anode base body, wherein the anode base body comprises a carrier metal and a precious metal-based active material.

20. The process of claim 19 wherein the screen is the fabric comprising an interwoven network of fibers.

21. The process of claim 20 he acidic electrolytic plating bath of claim 15 wherein the fabric is constructed from a polypropylene.

22. The acidic electrolytic plating bath of claim 20 wherein the fabric is constructed of material selected from the group consisting of fiberglass, glass wool, glass filament, and refractory ceramic fibers (RCF).

23. A process for electrolytic plating a metal deposit onto a substrate, the process comprising:

immersing the substrate into an electrolytic plating bath comprising:

a cathode;

an anode comprising a fabric screen disposed around and spaced apart from an anode base body comprising a carrier material and a precious metal-based active material; and

an electrolytic plating composition for acid Cu plating comprising a source of Cu ions to provide between about 4 g/L and about 70 g/L Cu ions, a source of chloride ions in an amount sufficient to provide between about 100 mg/L and about 300 mg/L chloride ions, and a source of a molybdenum ions sufficient to provide between about 200 mg/L and 1200 mg/L of molybdenum ions; and

supplying electrical current to the electrolytic plating bath to deposit Cu onto the substrate.

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