

(19)



(11)

EP 1 983 078 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

22.10.2008 Bulletin 2008/43

(51) Int Cl.:

C25D 3/66 (2006.01)

C25D 5/18 (2006.01)

(21) Application number: **07106339.0**

(22) Date of filing: **17.04.2007**

(84) Designated Contracting States:

**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IS IT LI LT LU LV MC MT NL PL PT RO SE
SI SK TR**

Designated Extension States:

AL BA HR MK RS

(71) Applicant: **Nederlandse Organisatie voor
toegepast-**

**natuurwetenschappelijk onderzoek TNO
2628 VK Delft (NL)**

(72) Inventor: **Van Erkel, Joost
7314 CN Apeldoorn (NL)**

(74) Representative: **van Loon, C.J.J.
Vereenigde
Johan de Wittlaan 7
2517 JR Den Haag (NL)**

(54) **Electrodeposition**

(57) The invention relates to a method for preparing an article which comprises a metal and/or a metalloid deposition, applied by electro-deposition, the method comprising

- providing a substrate (serving as a cathode) and an anode in a plating liquid, the plating liquid comprising (a) metal ions and/or metalloid ions to form the metallic layer and/or the metalloid layer and (b) an ionic liquid; and

- depositing the metal and/or metalloid on the substrate by applying an electrical potential between anode and substrate, wherein the electrical potential and/or electrical current are changed a plurality of times between at least one first value (A) and at least one second value different from said first value (B).

EP 1 983 078 A1

Description

[0001] The invention relates to a method wherein a metal or a metalloid is deposited on a substrate by electro-deposition. The invention further relates to an article provided with such a metal or metalloid.

[0002] A substrate may be provided with a metallic or metalloid for several purposes, *e.g.* a metallic or metalloid layer may be applied to improve the corrosion resistance of the substrate, as an intermediate layer for facilitating or improving the adherence of a subsequent functional layer to be applied to the substrate as a functional layer, such as a catalytically active layer, a layer for reflective electromagnetic radiation - for instance light - or to impart the substrate with a desirable visual appearance. A relatively thin functional layer may be applied on a substrate for economic and/or technical reasons. For instance a layer of a relatively expensive, lowly conductive and/or brittle functional metal (such as Ti) or metalloid may be applied to a substrate of a relatively cheap, highly conductive and/or stiff metal (*e.g.* steel or copper). Corrosion resistance can be improved by providing a layer of a suitable metal, such as a valve metal. Valve metals are metals that - when oxidised - form a dense metal oxide layer that has a low permeability to oxygen and/or water, such that it protects the metal covered by the oxide layer against corrosion. Such layer may also be referred to as a passivating oxide film. Examples of valve metals are titanium, hafnium, tantalum, aluminium, bismuth, zirconium, tungsten, niobium.

[0003] Well-known methods to provide a metal layer to a substrate include electro-deposition, cladding, welding or gluing of a metal layer to the substrate.

[0004] With cladding, welding or gluing techniques it is in general difficult to control the layer thickness and/or to provide a uniform metal layer thickness, in particular in case the layer to be applied should be thin and/or in case the surface of the substrate is three-dimensionally shaped (not flat). Especially, the presence of one or more protrusions, protuberances, recesses (*e.g.* holes), curves and/or edges in/on a surface of a substrate to be coated may be detrimental to a property of the layer applied with such a technique.

[0005] Also, adherence may be unsatisfactory. Further, such process may be complicated and/or difficult to automate.

[0006] Electrochemical deposition (also called electro-deposition or electroplating) of metals, alloys and metalloids involves the reduction of ions from an electrolyte solution. The technique is well-known for deposition of many metal and metalloid layer. In electro-deposition the substrate is placed in a suitable electrolyte containing the ions of the metal or metalloid to be deposited. The substrate must have an electron conductive layer which forms the cathode which is connected to the negative terminal of a power supply. The positive terminal is connected to a suitable anode. The thickness of the deposited layer is a function of the number of electrons (charge)

used in the electro-deposition process.

[0007] Electro-deposition from aqueous solutions is only possible for providing a layer of a metal or metalloid having a sufficiently high standard potential (also known as Nernst potential). The standard potential of the metal or metalloid should be higher than the standard potential of water to hydrogen, or the kinetic for the reduction of water to hydrogen at the surface of the metal or metalloid should be so slow that the metal can be plated even if its standard reduction potential is below 0 Volt. For instance the noble metals and copper are examples of the first category, while zinc, chromium and cadmium are within the second category of metals that can be plated from aqueous solutions. However, an aqueous solution is in general not suitable or at least not practical for deposition of a metal or metalloid with a low reduction potential, *e.g.*, an alkaline earth metal, such as barium.

[0008] For providing a layer of a metal or metalloid having a substantially lower reduction potential than the reduction potential of water to hydrogen, for instance a layer of a valve metal such as aluminium, electro-deposition from aqueous solution is not feasible.

[0009] Past attempts to form a (valve) metal layer making use of a nonaqueous plating solution have not lead to satisfactory protective layers. The deposited layers were found to be insufficiently homogenous and/or the maximum thickness that could be realised was limited due to (chemical) inhibition. For instance, for titanium a thickness of up to only a few nanometers was feasible.

[0010] The application of an intermediate metal layer is for instance relevant for the manufacture of devices which may be used in a chemical process, such as catalytic devices, electrodes, in particular electrodes for electrocatalytic processes or other electrochemical processes. Depending upon the application for which the device is intended, one or more factors such as sufficient dimensionally stability, conductivity, chemical stability, physical stability, ability to withstand severe anodic attack, corrosion resistance, manufacture performance, electrochemical performance, catalytic activity and/or catalytic selectivity, are important.

[0011] Devices made by a known method, in particular electrodes for electrochemical processes made by a known method, generally lack sufficient or desirable performance in one or more of the above factors, at least when used in an industrial setting.

[0012] In general, these materials cannot be used alone to produce electrodes with adequate electro-chemical performance under industrial operating conditions. Therefore it has been proposed to provide composite electrodes, comprising a catalytic coating on a metal base. An example thereof is the dimensionally stable anode (DSA), described in US 3,632,498. Herein a specific electrically conductive base is described with a coating of a mixed crystal material comprising an oxide of a film-forming metal, such as titanium oxide, and an oxide of a platinum group metal. A drawback of this electrode is the need to manufacture and operate the electrode under

strictly controlled conditions in order to avoid the formation of an insulating oxide layer of the film-forming metal, which would result in electro-chemical passivation of the anode with an excessive rise of the cell voltage (the potential between the anode and cathode) during use.

[0013] Further, an intermediate protective coating may be used to form a barrier against oxidation of an electrode base. In particular, for such purpose, factors such as satisfactory adherence, conductivity, impermeability to water and/or oxygen, resistance to oxidation, physical stability and/or chemical stability are important.

[0014] It has further been proposed to use polymeric materials in the production of electrodes, *e.g.* in US 4,118,294. This publication acknowledges that valve metal electrodes can evolve hydrogen at reasonably low over potentials, but are badly effected by adsorbed hydrogen atoms which migrate into the valve metal and form hydrides, causing expansion of the valve metal lattice, weakening of its structure and falling or peeling off of the electrocatalytic coating. This effect is known in the art as hydrogen embrittlement.

[0015] US 4,331,528 describes a dimensionally stable electrode wherein a layer of a non-stoichiometric oxide of a passive metal is provided on the electrode substrate, to prolong the life-time of an electrode.

[0016] Still, there is a need for an alternative method to provide substrates with a metallic layer, in particular for use in an electro-chemical process.

[0017] It is an object of the invention to provide a novel method for preparing an article comprising a substrate of which a surface is provided with a metallic or metalloid, in particular a metallic or metalloid layer. More in particular, it is an object to prepare an article suitable for use in an electrocatalytic process or another chemical process.

[0018] It is a further object to provide such a method which allows adequate control of the growth, thickness, density, continuity, integrity and/or an (electro)chemical property of the metal or metalloid deposited on a surface of a substrate.

[0019] It is a further object to provide an article, comprising a metallic deposition and/or a metalloid deposition, with satisfactory and optionally one or more improved properties such as mentioned above.

[0020] It is in particular an object of the invention to provide such article wherein the metallic/metalloid is deposited as a layer, more in particular a protective layer, to protect the part of the article provided with the metallic/metalloid layer against corrosion, wherein the article preferably is an electrode, and/or wherein the metallic/metalloid layer is a (electro)catalytically active layer.

[0021] One or more other objects which may be met in accordance with the invention are clear from the remainder of the description and/or claims.

[0022] It has now been found that one or more objects underlying the invention are met by depositing a metal and/or a metalloid to a substrate making use of a specific plating liquid and applying an electrical potential in a spe-

cific way.

[0023] Accordingly, the present invention relates a method for preparing an article which comprises a metal and/or a metalloid deposition, applied by electro-deposition, the method comprising

- providing a substrate (serving as a cathode) and an anode in a plating liquid, the plating liquid comprising (a) metal ions and/or metalloid ions to form the metallic layer and/or the metalloid layer and (b) an ionic liquid; and
- forming the deposition through reduction of the metal ions and/or metalloid ions on the substrate by applying an electrical potential between anode and substrate, wherein the electrical potential and/or electrical current are changed a plurality of times between at least one first value (A) and at least one second value different from said first value (B).

[0024] Typically, at least one of the values A respectively B is equal to or higher than the standard potential of the metal/metalloid ion which is to be reduced and deposited to form the metal/metalloid layer.

[0025] It is observed that in a method of the invention it is possible to first apply value A and thereafter value B or *vice versa*.

[0026] The term "or" as used herein means "and/or" unless specified other wise.

[0027] The term "a" or "an" as used herein means "at least one" unless specified other wise.

[0028] When referring to a moiety (*e.g.* a compound, an ion, an additive etc.) in singular, the plural is meant to be included. Thus, when referring to a specific moiety, *e.g.* "ion", this means "at least one" of that moiety, *e.g.* "at least one ion", unless specified otherwise.

[0029] In accordance with the invention the potential respectively current may be changed from

A) a substrate potential respectively current being sufficient to cause reduction of the metal ions and/or metalloid ions (to a non-ionic state) - *i.e.* a reducing potential/current - to

B) a substrate potential respectively current being insufficient to cause said reduction of the metal ions and/or metalloid ions - *i.e.* a non-reducing potential/current - which non-reducing potential/current may be an oxidising potential/current.

[0030] A reducing respectively non-reducing potential is dependent upon the metal ions and/or metalloid ions which are to be deposited, and conditions such as the temperature. A non-reducing/reducing potential respectively current, can be routinely determined based on the reduction potential of the specific metal or metalloid, optionally in combination with some routine experimentation.

[0031] In accordance with the invention it is also possible to change the electrical potential and/or the current

from

A) a substrate potential having a high absolute value sufficient to cause reduction of the metal ions or metalloid ions, respectively a current through the substrate having a high absolute value sufficient to cause reduction of the metal ions or metalloid ions, to B) a substrate potential having a low absolute value, yet sufficient to cause the growth of nuclei comprising the metal or metalloid, respectively a current through the substrate having a low absolute value, yet sufficient to cause the growth of nuclei comprising the metal or metalloid.

[0032] A suitable potential/ current for step A respectively B reducing respectively non-reducing potential is dependent upon the metal ions and/or metalloid ions from which the layer is formed, and conditions such as the temperature.

[0033] A non-reducing potential/current may be an oxidising potential/current, *i.e.* a potential/current sufficient to cause part of the deposited metal/metalloid to be oxidised. An oxidising potential/current may be useful to etch or polish the surface of the deposited metal/metalloid. This may be beneficial to a property of the finally deposited material.

[0034] A metal/metalloid may in particular be deposited at a surface of the substrate. The surface may be an outer surface or an inner surface, *e.g.* inside pores of a porous substrate or an inner surface of a substrate comprising another type of cavity.

[0035] In particular, the metal/metalloid may be deposited as a layer partially or fully covering an inner or an outer surface of a substrate.

[0036] A method of the invention, is in particular advantageous for providing a particular smooth, homogeneous and/or closed metallic or metalloid layer. It is possible to provide a layer which has a low number of gaps identifiable with (scanning electron) microscopy or is essentially free of such gaps.

[0037] In particular one or more of such properties may be provided under relatively mild conditions, such as at a relatively low temperature.

[0038] An advantage of a method in accordance with the present invention is that a metal or metalloid (layer) can be applied onto a large surface by means of, for instance, a roll-to-roll deposition process. Moreover, the method generally does not require to be operated by highly skilled personnel. Further, a method of the invention may be carried out using relatively simple equipment, without needing a high investment, in particular compared to vacuum deposition technologies.

[0039] In accordance with the invention it is possible to apply a layer to a substrate with satisfactory properties, in particular for the layer to be suitable as a corrosion resistant layer, and/or a (electro-)catalytically active layer. In particular, in a method of the invention one or more properties, such as continuity of the layer, may be im-

proved.

[0040] The invention allows the formation of a layer with satisfactory properties within a wide thickness range. The thickness may in particular be at least 1 nm, at least 10 nm, at least 100 nm, at least 1 μm , at least 10 μm or at least 100 μm . The thickness may in particular be up to 10 mm, up to 1 mm, up to 400 μm , up to 100 μm , up to 10 μm , up to 1 μm up to 100 nm or up to 10 nm.

[0041] The invention allows the formation of a highly continuous metallic or metalloid layer, also in case the layer is relatively thick.

[0042] The invention further relates to an article comprising a metallic or a metalloid deposition (such as a metallic or a metalloid layer), obtainable by a method of the invention.

[0043] The invention further provides an article with a highly homogenous and/or smooth layer. In particular, the invention relates to an article, and a method for preparing such article, wherein the number of crystal defects in the metallic layer or metalloid layer is $10^6/\text{m}^2$ or less, or $10^5/\text{m}^2$ or less. The number of such defects can be determined by scanning electron microscopy (SEM).

[0044] In an embodiment, the metallic or metalloid layer has a low permeability to a gaseous, vaporous or liquid component, such as water. For instance, the permeability to water may be less than 10^{-6} g water/ m^2/day . The permeability may be determined as described in US2006/147346.

[0045] The substrate usually is an article of which at least part of the surface is electrically conductive. In particular the substrate may comprise a metal surface, a metalloid surface, a (semi-)conductive inorganic oxide surface or an organic (semi-)conductive surface. At least when the electrical potential is applied, the substrate and anode are in electrical communication with each other, forming an electrochemical cell with the plating liquid.

[0046] In particular, the surface of the substrate upon which the metal or metalloid is deposited, may comprise a metal selected from the group of titanium, iron, copper, aluminium, nickel, silver, zinc, molybdenum, chromium, lead, platinum, palladium, gold, including mixtures thereof, such as alloys thereof, in particular brass or steel. The surface may comprise an electron conductive form of carbon (such as graphite).

[0047] The surface of the substrate may comprise another sufficiently electron conductive material, such as a semiconductor, a (semi-) conductive polymer, a metalloid or a conductive oxide, or a combination of two or more of these (semi-)conductors.

[0048] The conductive oxide may comprise one or more conductive oxides, selected from the group of zinc oxide, tin oxide and/or indium tin oxide. These are available in transparent forms. Preferably, the transparent conductive oxide layer comprises zinc oxide and/or tin oxide. More preferably, the transparent conductive oxide layer comprises tin oxide.

[0049] In particular, the substrate may be a substrate selected from the group of circuit boards, vessels (such

as reactor vessels), plates, tubes, pipes, sheets, electrodes, foils, bars and bus-bars.

[0050] In an advantageous embodiment, a substrate of a relatively cheap material, e.g. copper, is used upon which a layer of a relatively expensive material, such as titanium, tantalum, gold, silver or a metal from the platinum group is deposited. Thus, an efficient catalytic device can be made of which only the surface (at which the catalyst is only needed) is provided with the expensive material.

[0051] In an advantageous embodiment, the substrate comprises a material with one or more desirable mechanical properties for a specific purpose, for instance steel or brass, but undesirable (electro-)chemical stability or another undesirable property for use in a specific application. The invention allows the provision of a protective metallic or metalloid layer on the substrate, to combine an advantageous mechanical property of the substrate, for instance a vessel or piping for use in a chemical process, with an advantageous chemical resistance (e.g. against corrosion) provided by the metallic or metalloid layer.

[0052] Prior to the plating, the substrate may be pre-treated in a manner known in the art for electro-plating. In particular contaminants and/or films may be removed from the substrate. The pre-treatment may in particular comprise a chemical cleaning step, such as an electrochemical cleaning step and or a physical cleaning step. Suitable pre-treatment steps are known in the art, and are, e.g. described in Dexter D. Snyder "Preparation for Deposition", chapter 23 in M. Schlesinger, M. Paunovic (eds), "Modern Electroplating", Electrochemical Society Series, 4th Edition, 2000, John Wiley & Sons, New York.

[0053] The invention allows the preparation of an article comprising a metallic or metalloid deposition (such as a layer) wherein a property of the deposition, such as thickness, density, structure, continuity or the like can be adequately controlled by selecting the electro-deposition conditions, in particular with respect to the changing voltage or current.

[0054] The voltage/current during the electro-plating process may be performed at galvanostatic control (current control), potentiostatic (potential control, using the potential difference over the substrate and a reference electrode, or at cell voltage control (*i.e.* wherein the potential over the substrate and anode (counter electrode) is controlled).

[0055] Parameters that can be controlled to adjust properties of the deposition include cell voltage, cathode potential, and current conditions. More specifically, by choosing the duration of the electro-deposition and total charge (coulombs) applied for the duration of the electro-deposition, and in particular by choosing the plating conditions with respect to frequency by which the current/potential is changed, duration of the steps A respectively B, value of (absolute maximum of) "reducing voltage/current" respectively "non-reducing voltage/current", slope by which the voltage/current is changed.

[0056] In accordance with the invention, usually at least for a part of the duration of the applying of the electrical potential, the potential of the substrate is below the reduction potential of the metal ions and/or metalloid ions in the plating liquid which are to be deposited on the substrate.

[0057] A non-reducing voltage/current may be 0. Accordingly, the cell may be let at the open cell voltage, or at the rest potential for a period of time.

[0058] A non-reducing voltage/current may have the opposite sign of charge from the (current at the) reduction potential. Hereby a part of the deposited metal/metalloid may be reoxidised and optionally dissolved. Thus, such voltage/current should be such that - on average - reduction and deposition is larger the oxidation and dissolution.

[0059] In a method of the invention, the ratio of the current in step B to the current in step A (wherein current and potential are taken as their absolute value) is less than 1. Usually said ratio is less than 0.9. Preferably said ratio up to 0.8, in particular up to 0.6, more in particular up to 0.5.

[0060] The ratio of the current in step B to the current in step A (absolute values) is at least 0.

[0061] The current in step B (non-reducing current) may be an oxidising current (to redissolve part of the deposited metal or metalloid), as long as on average the amount of redissolved metal or metalloid is less than the amount of deposited metal or metalloid. It is also possible to change between a high reducing current and a low reducing current, wherein the low reducing current can be advantageous to allow growth of nuclei of the metal or metalloid.

[0062] The frequency of changing the potential/current can be chosen within wide limits. The frequency may be essentially constant or varied.

[0063] Usually, the average frequency of the changing (to get from a first reducing potential/current to the next reducing potential/current) is at least 0.01 Hz, in particular at least 0.1 Hz or at least 1 Hz. The average frequency of the changing is usually up to 10 KHz, in particular up to 1 KHz or up to 500 Hz.

[0064] The number of changes (the number of cycles from a step A to the next step A, or the number of cycles from a step B to the next step B) may be chosen within wide limits, depending upon factors, such as the desired amount of deposition (such as the desired layer thickness), the current density applied, the frequency, the deposition efficiency, the optional use of an etching potential/current. The skilled person will be able to determine a suitable number, based upon the information disclosed herein, common general knowledge and optionally some routine testing. The number of changes from A to B or B to A usually is more than 2, and in particular it may be at least 5, at least 10 or at least 25.

[0065] The upper limit is determined by reaching the target deposition (such as reaching a specific thickness of a metallic/metalloid layer). It may for instance be up to 1000, up to 100 000 or up to 1 000 000. However a

higher number of changes is in principle allowed, in particular in case the changing frequency is high.

[0066] Figure 1A-C shows a number of ways by which the current/potential can be changed. It will be understood that other possibilities may be employed, e.g. two or more of the ways of changing may be combined. Herein, Level II is a reduction current/potential at which deposition takes place. Level I can be a) a 0 current or rest potential (open circuit potential); b) an anodic current/potential at which a part of the previously deposited metal or metalloid may be (oxidised and) dissolved; c) a relatively low reduction current/potential (compared to Level II) which may be used to grow metal/metalloid nuclei, which are formed in a previous Level II current/potential. In these Figures, t_1 is the cycle time from a first Level I to the next (the reciprocal of the frequency), t_2 the duration of the current/potential at level II, t_3 the duration at level I, and t_4 respectively t_5 the time to change from (an extreme) current/potential from one level to the other, in case the current/voltage change is effected with a specific slope. The ratio of t_2/t_1 may be chosen within wide limits. A relatively high ratio may be advantageous from a processing time of view. The ratio t_2/t_1 may in particular be at least 0.001, at least 0.01, or at least 1. The ratio t_2/t_1 may in particular be up to 1000, up to 100 or up to 10.

[0067] In an embodiment of the invention, the changing comprises applying current/potential pulses, e.g. as shown in Figure 1A. Herein, the current/potential is changed essentially instantaneously.

[0068] In an embodiment, the change from a first current/potential to another takes places at a specific rate, e.g. as shown in Figure 1B.

[0069] In an embodiment, the changing comprises applying current/potential in an undulating way, for instance by a sinusoidal change, e.g. as shown in Figure 1C.

[0070] Further, the temperature may be controlled. Typically, the temperature is at least above the melting temperature of the ionic liquid / salt system. For practical reasons, the temperature is preferably at least ambient temperature, such as at least 20 °C or at least 25 °C. An elevated temperature, e.g. of at least 30 °C, at least 40 °C or at least 50 °C may be chosen in case a plating liquid to be used is not sufficiently liquid at ambient temperature. A relatively high temperature is usually advantageous for achieving a relatively low viscosity and/or a improved electrical conductance of the liquid.

[0071] Selecting a temperature within a specific range, may be used for a (further) improved smoothness of the layer.

[0072] Usually the temperature is up to 200 °C. For practical reasons, it may be preferred that the temperature is up to 100 °C, up to 70 °C or up to 50 °C.

[0073] Further, electro-deposition may be carried out with or without convection of the liquid, for instance with or without agitation. Convection is considered advantageous in order to avoid or at least reduce the occurrence of a possibly detrimental concentration gradient of the ions to be deposited at the cathode.

[0074] The plating liquid comprises an ionic liquid. An ionic liquid is a liquid formed of a salt that is liquid under the process conditions, such as a melt of a salt. In general an ionic liquid used in a method of the invention, has a melting point below 200 °C, preferably of 100 °C or less, in particular of 50 °C or less. It is in particular preferred that the ionic liquid is liquid at about 20 °C or at about 25 °C. Such liquid may be referred to as a room temperature liquid salt.

[0075] Salts that form an ionic liquid are known in the art. For instance, US-A 4,764,440 discloses a composition comprising a mixture of a metal halide and a hydrocarbyl-saturated onium salt, wherein at least one of the hydrocarbyl groups is an aromatic hydrocarbyl group. The contents of this publication with respect to the description of suitable ionic liquids, in particular as specified in the claims thereof is incorporated herein by reference. US-A 5,731,101 discloses an ionic liquid composition comprising a mixture of a metal halide and an alkyl-containing amine hydrohalide salt of the formula $R_3 N.HX$, where at least one R is alkyl and X is halogen, which amine hydrohalide salt contains either one or two alkyl groups therein. The contents of this publication with respect to the description of suitable ionic liquids, in particular as specified in the claims thereof is incorporated herein by reference.

[0076] US-A 5,892,124 discloses liquid salts of the general formula Q^+A^- , wherein Q^+ represents quaternary ammonium or phosphonium, and A^- represents various anions including tetrachloroaluminate and trichlorozincate. The contents of this publication with respect to the description of suitable ionic liquids, in particular as specified in the claims thereof is incorporated herein by reference.

[0077] In particular suitable is an ionic liquid selected from the ionic liquids described in WO 02/26381, of which the contents of this publication with respect to the description of suitable ionic liquids, in particular as specified in the claims thereof is incorporated herein by reference. Such ionic compound can be formed by the reaction of at least one amine salt of the formula $R^1R^2R^3R^4N^+X^-$ (I) with at least one hydrated salt, which is a chloride, nitrate, sulphate or acetate of Li, Mg, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb, Bi, La or Ce; wherein R^1 , R^2 and R^3 are each independently a C_1 to C_5 alkyl or a C_6 to C_{10} cycloalkyl group, or wherein R^2 and R^3 taken together represent a C_4 to C_{10} alkylene group, thereby forming with the N atom of formula I a 5 to 11 membered heterocyclic ring, and wherein R^4 is hydrogen, or phenyl, or a C_1 to C_{12} alkyl or cycloalkyl group, optionally substituted with at least one group selected from OH, Cl, Br, F, I, phenyl, NH_2 , CN, NO_2 , $COOR^5$, CHO, COR^5 and OR^5 , wherein R^5 is a C_1 to C_{10} alkyl or cycloalkyl group, and X^- is an anion capable of being complexed by the said hydrated salt, for instance a halogen ion, such as Cl^- or Br^- .

[0078] In an embodiment, the ionic liquid comprises a salt of the following cations and/or anions:

- cations selected from the group of monosubstituted imidazolium compounds, disubstituted imidazolium compounds, trissubstituted imidazolium compounds, pyridinium compounds, pyrrolidinium compounds, phosphonium compounds, ammonium compounds, guanidinium compounds and isouronium compounds, including combinations thereof. The substituents may in particular be selected from the substituents described above, when referring to R^1 - R^5 in the amine salt of the formula $R^1R^2R^3R^4N^+X^-$ (I).
- anions selected from the group of chloride, bromide, iodide, nitrate, nitrite, fluoride, phosphate, imide, amide, borate, tosylate, tetrafluoroborate, hexafluoroborate, hexafluorophosphate, trifluoromethanesulfonate, methylsulfate, bis(pentafluoroethyl)phosphinate, thiocyanate, octylsulfate, hexylsulfate, butylsulfate, ethylsulfate, dicyanamide, hexafluoroantimonate, bis-(pentafluoroethyl)phosphinate, bis-(trifluoromethyl)imide, trifluoroacetate, bis-trifluorsulfonimide, triflate and dicyanamide, including combinations thereof.

[0079] The plating liquid may comprise a solvent, solvents being materials other than the liquid salt which are liquid under the conditions at which the method is carried out. In particular, the solvent may be chosen from inorganic solvents other than water and organic solvents, such as benzene or an alcohol.

[0080] In case the reduction potential of the metal/metalloid is sufficiently high, water may be present. The skilled person will be able to determine this based on common general knowledge.

[0081] The solvent concentration will usually be less than 25 wt. %, based on total liquid salt, in particular 20 wt. % or less, more in particular 15 wt. %wt or less. Preferably, the solvent concentration is up to 2 wt. % based on total liquid salt, more preferably less than 1 wt. %.

[0082] In a much preferred embodiment the plating liquid is essentially free of water and/or other solvents. A plating liquid is in particular considered to be essentially free of a solvent if the concentration of that solvent is less than 0.5 wt. %, based on total liquid salt, more in particular less than 0.1wt. % of a solvent, or less than 0.01 wt. %.

[0083] The metal/metalloid ions for forming the metallic/metalloid deposition (such as a layer), may in particular be any metal ion or metalloid ion that can be reduced from ionic state to non-ionic state (atomic state). The ions may all be of the same metal or metalloid, or a combination of two or more ions selected from the group of metal ions and metalloid ions may be used.

[0084] A metallic deposition (such as a layer) as used herein is a deposition comprising one or more metals, thus the term includes depositions of a metallic alloy. In particular a deposition is considered metallic if it shows metallic electrical conductance.

[0085] In particular, the ions may be selected from valve metals and catalytically active metals, such as metals from the platinum group. Preferred metal ions include

ions selected from the group of titanium, tantalum, aluminium, hafnium, bismuth, zirconium, tungsten, niobium, chromium, manganese, zinc, silver, gold, platinum and palladium, ruthenium, including combinations thereof, in particular alloys thereof. Particularly preferred is at least one metal ion selected from titanium, aluminium and tantalum.

[0086] Metalloids are elements that are generally not considered real metals, but that do show more or less metallic behaviour in one or more specific aspects. In particular, metalloids are capable of conducting electricity, to the extent that they are semiconductors rather than metallic conductors. In particular, Boron (B), Silicon (Si), Germanium (Ge), Arsenic (As), Antimony (Sb), Tellurium (Te) and Polonium (Po) are examples of metalloids. Of these, silicon and/or germanium are preferred examples of metalloids, to be deposited on a substrate in accordance with the invention.

[0087] A metalloid deposition (such as a layer) as used herein is a deposition comprising one or more metalloids, thus the term includes depositions of a metalloid alloy. In particular such a deposition is considered a metalloid deposition if it shows metalloid electrical conductance (i.e. showing semi-conductive properties, such as a semi-metal).

[0088] The counter ions of the metal ions or metalloid used for deposition may be the same or different from the cations of the ionic liquid. In particular the counter ions may be chosen from the group of chloride, bromide, iodide, nitrate, nitrite, fluoride, phosphate, imide, amide, borate, tosylate, tetrafluoroborate, hexafluoroborate, hexafluorophosphate, trifluoromethanesulfonate, methylsulfate, bis(pentafluoroethyl)phosphinate, thiocyanate, octylsulfate, hexylsulfate, butylsulfate, ethylsulfate, dicyanamide, hexafluoroantimonate, bis-(pentafluoroethyl)phosphinate, bis-(trifluoromethyl)imide, trifluoroacetate, bis-trifluorsulfonimide, triflate and dicyanamide, including combinations thereof.

[0089] In an embodiment of the invention, a deposition (such as a layer) of an alloy is formed by using co-deposition. This may be achieved by using a single plating liquid comprising more than one type of ions to be deposited on the substrate, to allow co-deposition to take place in a single electro-deposition process.

[0090] In an embodiment, the different ions to be deposited are dissolved in separate plating liquids, with which the substrate is sequentially contacted under plating conditions. This allows the formation of different layers on top of each other.

[0091] The total concentration of the salt comprising the ions for forming the metallic/metalloid layer preferably is at least 0,1 mol%, more preferably at least 1 mol%, even more preferably at least 5 mol%, or at least 10 mol%. A relatively high concentration is in particular advantageous in order to allow a high deposition speed.

[0092] The upper limit is in particular determined by the maximum allowable concentration in order to maintain the plating liquid in a liquid state (the saturation level).

A relatively high concentration usually advantageous for a high deposition rate. Also, this allows for a relatively large amount of ions can usually to be reduced and deposited before depletion of the liquid may become noticeable. Also the presence of the ions to be deposited in a relatively high concentration may be advantageous for improved liquidity (reduced viscosity, reduced melting temperature of the liquid), and/or improved electrical conductance.

[0093] The total concentration of the salt of the metal/metalloid ions for forming the metallic/metalloid deposition (such as a layer) preferably is up to 70 mol %, more preferably up to 65 mol %, in particular up to 60 mol%. For practical reasons, e.g. reaching saturation in the liquid, a lower concentration may be chosen, e.g. up to 40 mol %, up to 20 mol %, up to 10 mol %, or 5 mol % or less.

[0094] In an advantageous embodiment, a "sacrificial electrode" is used as a counter electrode (anode). At least the surface of such an electrode comprises the same metal or metalloid as the metal or metalloid that is to be deposited on the substrate. While the metal or metalloid is deposited on the substrate during electro-deposition, metal/metalloid at a surface of the sacrificial electrode will be oxidised and dissolve in the plating liquid. Thus, the composition of the plating liquid can be maintained at about the same concentration for a prolonged time, or at least depletion of the liquid with metal/metalloid ions can be postponed. Such electrode may for instance be a plate, foil or thread of the metal/metalloid to be deposited, e.g. an aluminium counter electrode can be used when depositing aluminium on a substrate from a aluminium ions containing ionic liquid electrolyte.

[0095] The plating liquid may further comprise one or more additives, such as a brightener and/or a surface active agent. One or more additives are optionally also deposited. Suitable conditions for the additives are e.g. described in "Effect of additives", Chapter 10 in M. Schlesinger, M. Paunovic (eds), "Fundamentals of Electrochemical Deposition", Electrochemical Society Series, 2nd Edition, 2006, John Wiley & Sons, New York, of which Chapter the contents are incorporated by reference.

[0096] After forming the metallic/metalloid deposition (such as a layer), the article may be subjected to one or more post-treatment steps. For instance, excess ionic liquid may be removed from the article.

[0097] The invention will now be illustrated by the following examples.

Example 1 (reference):

Aluminium deposition at constant current density

[0098] The substrate properties were as follows: $\sim 1\text{cm}^2$ Si(100) crystal coated with $\sim 5\text{nm}$ Chromium (adherence layer) and $\sim 200\text{nm}$ gold (surface layer upon which aluminium is deposited).

[0099] As a Counter Electrode: Aluminium-sheet

99,99% Al $\sim 6\text{cm}^2$ was used.

[0100] As a reference electrode: Aluminium-wire diameter 0,5mm 99,99% Al was used.

[0101] The ionic liquid was 1-Ethyl-3-methyl-imidazoliumchloride (EMImCl) (40 mol %) comprising Aluminium chloride (AlCl_3) (60mol%).

[0102] The process conditions were as follows:

Current density: -10 mA/cm^2 constant current

Temperature: 30°C

Deposition time: 30 seconds (deposition charge $Q = t \times j = 0,3\text{ C/cm}^2$, corresponding to a deposition of a layer having a thickness of about 100 nm (calculated)).

[0103] The results were as follows:

Layer thickness measured $\sim 130\text{nm}$ (profilometer)

Average Roughness $\sim 26\text{ nm}$ (profilometer)

The deposited layer was also inspected visually. The layer was found to be white dull/mat with clearly inhomogeneous areas, in particular at the edges.

Example 2

Aluminium deposition using pulsed current density

[0104] Using the same type of substrate and plating liquid, electro-deposition was carried out using a pulsed current, as schematically shown in Figure 1A.

[0105] I_1 : 0 mA/cm^2 , I_{II} : -100mA/cm^2 , t_1 : 0,11s, t_2 : 0,01s, t_3 : 0,1s. Deposition takes place during t_2 .

[0106] Temperature: 30°C

[0107] Deposition time (total duration of experiment): 33 seconds (deposition charge $Q = t \times j = 0,3\text{ C/cm}^2$, corresponding to a deposition of a layer having a thickness of about 100nm (calculated))

[0108] Layer thickness measured $\sim 100\text{ nm}$ (profilometer)

[0109] Average Roughness $\sim 7\text{ nm}$ (profilometer)

[0110] Visual evaluation revealed that the deposited layer was lustrous and homogenous also at the edges.

Example 3:

Aluminium deposition using pulsed current density

[0111] Example 2 was repeated, but with t_1 : 0,2s, t_2 : 0,1s, t_3 : 0,1s and a deposition time of 6 seconds to realise the same deposition charge ($0,3\text{ C/cm}^2$)

[0112] The results were as follows.

[0113] Layer thickness measured $\sim 100\text{ nm}$ (profilometer)

[0114] Average Roughness $\sim 1,5\text{ nm}$ (profilometer)

[0115] Visual evaluation revealed that the deposited layer was lustrous and homogenous also at the edges.

[0116] The adherence of the layer was tested with the so called scotch tape test and found to be excellent.

Example 4:

pulsed deposition on glas/ITO/PEDOT

[0117] A substrate of $\sim 1\text{cm}^2$ glass coated with ITO (Indium tin oxide, a transparent conducting oxide layer) which ITO in turned had been provided with a Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT) layer (a few nm). Aluminium was deposited on the PEDOT layer.

[0118] The counter Electrode was aluminium-sheet 99,99% Al $\sim 6\text{ cm}^2$.

[0119] The reference electrode was aluminium-wire diameter 0,5mm 99,99% Al.

[0120] Ionic liquid was 1-Ethyl-3-methyl-imidazolium-chloride (EMImCl, 40 mol%) comprising aluminiumchloride (AlCl_3 , 60mol%)

[0121] The process conditions were as follows.

[0122] A pulsed current was used as schematically shown in Figure 1A, with I_1 : 0 mA/cm², I_2 : -20mA/cm², t_1 : 0,2s, t_2 : 0,1s, t_3 : 0,1s.

[0123] Temperature: 30 °C

[0124] Deposition time was 30 seconds (deposition charge $t \times j = 0,3\text{ C/cm}^2$, corresponding to a calculated layer thickness of 100nm)

[0125] After deposition the article was visually evaluated: the deposited layer was mat to lustrous and homogenous, also at the edges.

Claims

1. A method for preparing an article which comprises a metal deposition and/or a metalloid deposition, applied by electro-deposition, the method comprising

- providing a substrate (serving as a cathode) and an anode in a plating liquid, the plating liquid comprising (a) metal ions and/or metalloid ions to form the metallic layer and/or the metalloid layer and (b) an ionic liquid; and
- forming the deposition through reduction of the metal ions and/or metalloid ions on the substrate by applying an electrical potential between anode and substrate, wherein the electrical potential and/or electrical current are changed a plurality of times between at least one first value (A) and at least one second value different from said first value (B).

2. A method according to claim 1, wherein the electrical potential and/or the current is changed from

- A) a substrate potential respectively current being sufficient to cause reduction of the metal ions and/or metalloid ions to their non-ionic state (*i.e.* a reducing potential/current), to
- B) a substrate potential respectively current be-

ing insufficient to cause reduction of the metal ions and/or metalloid ions to their non-ionic state (*i.e.* a non-reducing potential/current).

3. A method according to claim 1 or 2, wherein the electrical potential and/or the current is changed from

A) a substrate potential having a high absolute value sufficient to cause reduction of the metal ions and/or metalloid ions to their non-ionic state, respectively a current through the substrate having a high absolute value sufficient to cause reduction of the metal ions and/or metalloid ions to their non-ionic state, to

B) a substrate potential having a low absolute value, yet sufficient to cause the growth of nuclei comprising the metal and/or metalloid, respectively a current through the substrate having a low absolute value, yet sufficient to cause the growth of nuclei comprising the metal or metalloid.

4. Method according to any of the preceding claims, comprising changing the current and/or potential to a value sufficient to oxidise a part of the metal and/or metalloid that has been deposited.

5. Method according to any of the preceding claims, wherein the average frequency of the change (from a first reducing potential/current "A" to the next reducing potential/current "A") is in the range of 0.01 Hz to 10 kHz, in particular in the range of 0.1 Hz to 1 kHz.

6. Method according to any of the preceding claims, wherein the absolute value of the ratio of the current in step B to the current in step A is 0 to 0.9, preferably 0 to 0.7, in particular 0 to 0.5.

7. Method according to any of the preceding claim, wherein the changing comprises making intervals in the applied potential and/or current, applying potential and/or current pulses, and/or applying an undulating potential and/or current.

8. Method according to any of the preceding claims, wherein the metal ions or metalloid ions are selected from the group of ions of tantalum, titanium, aluminium, bismuth zirconium, tungsten, niobium, hafnium, chromium, manganese, zinc, silver, gold, platinum, palladium, ruthenium, Boron, Silicon, Germanium, Arsenic, Antimony, Tellurium (Te) and Polonium (Po) including combinations thereof.

9. Method according to any of the preceding claims, wherein the ionic liquid comprises a salt, liquid under the process conditions, selected from salts formed of

- at least one of the cations from the group of monosubstituted imidazolium derivatives, disubstituted imidazolium derivatives, trissubstituted imidazolium derivatives, pyridinium derivatives, pyrrolidinium derivatives, phosphonium derivatives, ammonium derivatives, guanidinium derivatives and isouronium derivatives. 5
- and at least one of the anions from the group of chloride, bromide, iodide, nitrate, nitrite, fluoride, phosphate, imide, amide, borate, tosylate, tetrafluoroborate, hexafluoroborate, hexafluorophosphate, trifluoromethanesulfonate, methylsulfate, bis(pentafluoroethyl)phosphinate, thiocynate, octylsulfate, hexylsulfate, butylsulfate, ethylsulfate, dicyanamide, hexafluoroantimonate, bis-(pentafluoroethyl)phosphinate, bis-(trifluoromethyl)imide, trifluoroacetate, bis-trifluorsulfonimide, triflate and dicyanamide. 10 15
- 10.** Method according to any of the preceding claims, wherein the ionic liquid comprises a salt, liquid under the process conditions, selected from salts formed by the reaction of at least one amine salt of the formula $R^1R^2R^3R^4N^+X^-(I)$ with at least one hydrated salt, which is a chloride, nitrate, sulphate or acetate of Li, Mg, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb, Bi, La or Ce; wherein R^1 , R^2 and R^3 are each independently a C_1 to C_5 alkyl or a C_6 to C_{10} cycloalkyl group, or wherein R^2 and R^3 taken together represent a C_4 to C_{10} alkylene group, thereby forming with the N atom of formula I a 5 to 11 membered heterocyclic ring, and wherein R^4 is hydrogen, or phenyl, or a C_1 to C_{12} alkyl or cycloalkyl group, optionally substituted with at least one group selected from OH, Cl, Br, F, I, phenyl, NH_2 , CN, NO_2 , $COOR^5$, CHO, COR^5 and OR^5 , wherein R^5 is a C_1 to C_{10} alkyl or cycloalkyl group, and X^- is an anion capable of being complexed by the said hydrated salt. 20 25 30 35
- 11.** Method according to any of the preceding claims, wherein a metallic layer and/or a metalloid layer comprising is formed at a surface of the substrate by the electro-depositing. 40
- 12.** Method according to any of the preceding claims wherein the metal or metalloid is deposited on a surface of the substrate, the surface comprising a metal, a (semi-)conductive organic material and/or a conductive oxide. 45 50
- 13.** Method according to any of the preceding claims, wherein the substrate is an item selected from the group of circuit boards, vessels (such as reactor vessels), plates, tubes, pipes, sheets, electrodes, foils, bars and bus bars. 55
- 14.** Article comprising a metallic layer and/or metalloid layer, obtainable by any of the preceding claims.
- 15.** Article according to claim 14, wherein the number of crystal defects in the deposited layer is $10^6/m^2$ or less.

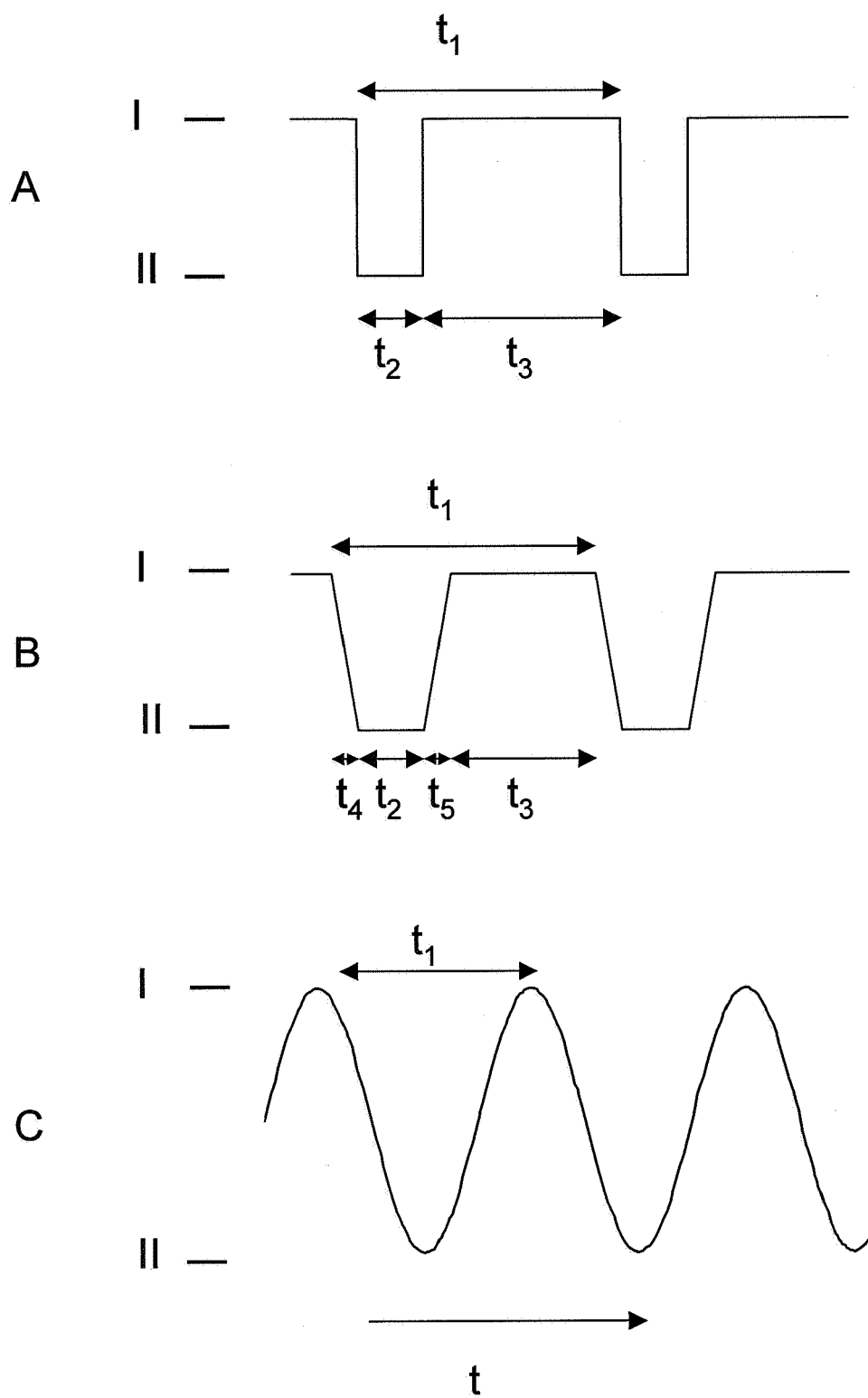


Figure 1



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 07 10 6339

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	DE 101 08 893 A1 (HEMPELMANN ROLF [DE]) 24 October 2002 (2002-10-24) * claims 1-7,10-13; examples 9-11 * * page 1, lines 18-31 * * page 3, lines 2-15 * -----	1-15	INV. C25D3/66 C25D5/18
X	US 4 966 660 A (SETSUKO TAKAHASHI [JP] ET AL) 30 October 1990 (1990-10-30) * claim 1; example 6 * * page 4, lines 29-37 * * page 5, lines 12-17 * -----	1-15	
X	WO 2006/053362 A (PLANSEE SE [AT]; EICHEM KOMPETENZZENTRUM FUER AN [AT]; SCHOTTENBERGER H) 26 May 2006 (2006-05-26) * claims 1,2,11,12,20,25,31 * * page 12, lines 10-23 * * page 13, lines 12-15 * -----	1-15	
			TECHNICAL FIELDS SEARCHED (IPC)
			C25D
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 17 September 2007	Examiner Gault, Nathalie
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

3
EPO FORM 1503 03/82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 07 10 6339

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

17-09-2007

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
DE 10108893	A1	24-10-2002	NONE		

US 4966660	A	30-10-1990	EP	0323520 A1	12-07-1989
			WO	8900616 A1	26-01-1989

WO 2006053362	A	26-05-2006	NONE		

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US 3632498 A [0012]
- US 4118294 A [0014]
- US 4331528 A [0015]
- US 2006147346 A [0044]
- US 4764440 A [0075]
- US 5731101 A [0075]
- US 5892124 A [0076]
- WO 0226381 A [0077]

Non-patent literature cited in the description

- Modern Electroplating. Electrochemical Society Series. John Wiley & Sons, 2000 [0052]
- Effect of additives. Fundamentals of Electrochemical Deposition", Electrochemical Society Series. John Wiley & Sons, 2006 [0095]