The present invention relates to an aqueous plating bath composition and a method for depositing a palladium layer by electroless plating onto a substrate. The aqueous plating bath composition according to the present invention comprises a source for palladium ions, a reducing agent for palladium ions and an aldehyde compound. The aqueous plating bath composition has an increased deposition rate for palladium while maintaining bath stability. The aqueous plating bath composition has also a prolonged life time. The aldehyde compounds of the present invention allow for adjusting the deposition rate to a constant range over the bath life time and for electrolessly depositing palladium layers at lower temperatures. The aldehyde compounds of the present invention activate electroless palladium plating baths having a low deposition rate and reactivation aged electroless palladium plating baths.
Plating bath composition and method for electroless plating of palladium

Field of the Invention

The present invention relates to aqueous plating bath compositions and methods for electroless plating of palladium in the manufacture of printed circuit boards, IC substrates and for metallization of semiconductor wafers.

Background of the Invention

Electroless deposition of palladium in the manufacture of printed circuit boards, IC substrates and the like as well as metallization of semiconductor wafers is an established technique. The palladium layers are used for example as barrier layers and/or wire-bondable and solderable finishes.

Electroless palladium plating bath compositions comprising a source for palladium ions, a nitrogenated complexing agent and a reducing agent selected from formic acid and derivatives thereof are disclosed in US 5,882,736. Such electroless palladium plating bath compositions are suited to deposit pure palladium in contrast to plating bath compositions containing hypophosphite as reducing agent which result in palladium-phosphorous alloy layers.

US patent 4,424,241 describes an electroless plating solution comprising palladium, organic ligands and reducing agents, i.a. formaldehyde and formic acid.
The reducing agents are used in high concentrations. According to US patent 4,424,241 concentrations too low slow the deposition rate.

Although much of the prior art literature teaches palladium plating bath compositions, the plating rates obtained therewith cannot satisfy the current need for steadily increasing plating rates that are required in order to achieve economic manufacturing.

Further, the deposition rate constantly decreases during bath life and a deposition rate too low finally terminates the life time of an electroless palladium plating bath. This is due to the catalytic effect of already deposited palladium and the autocatalytic deposition mechanism. Usually, changing the temperature of an electroless palladium plating bath is used for regulating the deposition rate and duration of bath life. Increasing the bath temperature also increases the deposition rate. But operating the bath at a higher temperature simultaneously increases the risk of destabilising the bath.

The stability of such a plating bath means that the plating bath is stable against decomposition, i.e. the undesired precipitation of metallic palladium in the plating bath itself. Accordingly, destabilising an electroless palladium plating bath in turn shortens the bath life. Due to the high price of palladium early discarding of an electroless palladium plating bath is undesired for economic reasons as well.

**Objective of the present Invention**

It is an objective of the present invention to provide a plating bath composition and a method for electroless plating of palladium wherein the deposition rate is further increased. It is a further objective of the present invention to provide a plating bath composition and a method for electroless plating of palladium which allow for adjusting the deposition rate to the desired high value. It is a further objective of the present invention to provide a plating bath composition and a method for electroless plating of palladium wherein the deposition rate is further
increased while the bath remains still stable. It is a particular objective of the present invention to provide a plating bath composition and a method for electroless plating of palladium which allow for maintaining a constant high deposition rate during the life time of the plating bath. It is a further objective of the present invention to provide a plating bath composition and a method for electroless plating of palladium which allow for increasing the life time of the plating bath.

**Summary of the Invention**

These objectives are solved with an aqueous plating bath composition for electroless deposition of palladium, comprising

(i) at least one source for palladium ions,

(ii) at least one reducing agent for palladium ions, and

(iii) at least one aldehyde compound according to Formula (I)

\[
\text{H}_2\text{C}=\text{O}
\]

**Formula (I)**,

wherein R is selected from the group consisting of -H; unsubstituted or substituted, linear alkyl groups comprising 1 to 10 carbon atoms; and unsubstituted or substituted, branched alkyl groups comprising 3 to 10 carbon atoms; and unsubstituted or substituted aryl groups; and

wherein the at least one aldehyde compound according to Formula (I) has a concentration ranging from 0.01 to 25 mg/l.

These objectives are further solved by a method for electroless palladium plating comprising the steps of

(a) providing a substrate,
(b) contacting the substrate with the aqueous plating bath composition as described above and thereby depositing a layer of palladium onto at least a portion of the substrate.

The aqueous plating bath composition according to the present invention is called the composition or the composition according to the present invention herein. The terms "plating" and "depositing" are used interchangeably herein.

The aldehyde compounds according to Formula (I) provide the aqueous plating bath composition according to the present invention with an increased deposition rate for palladium, in particular for pure palladium, and a prolonged life time. Although increasing the deposition rate, the aldehyde compounds according to Formula (I) do not impair the stability of the aqueous plating bath composition according to the present invention against undesired decomposition. Adding the aldehyde compounds according to Formula (I) to an electroless palladium plating bath allows for adjusting the deposition rate to a constant range over the bath life time. The aldehyde compounds according to Formula (I) of the present invention activate electroless palladium plating baths having a low deposition rate even when freshly prepared and reactivate aged electroless palladium plating baths. The aldehyde compounds according to Formula (I) of the present invention allow for electrolessly depositing palladium layers at lower temperatures.

**Brief Description of the Figures**

Figure 1 shows the deposition rate of an aqueous plating bath composition containing formaldehyde.

Figure 2 shows the deposition rate of an aqueous plating bath composition containing n-propanal.
Figure 3 shows the deposition rate of an aqueous plating bath composition containing n-pentanal in a concentration range of 0.25 to 1.25 mg/l.

Figure 4 shows the deposition rate of an aqueous plating bath composition containing n-pentanal in a concentration range of 1 to 10 mg/l.

**Detailed Description of the Invention**

The aqueous plating bath composition comprises (iii) at least one aldehyde compound according to Formula (I)

\[
\begin{align*}
\text{R} & \quad \text{C} \quad \text{H} \\
\text{O} & \quad \text{Formula (I)},
\end{align*}
\]

wherein \( R \) is selected from the group consisting of \(-\text{H}\); unsubstituted or substituted, linear alkyl groups comprising 1 to 10 carbon atoms; and unsubstituted or substituted, branched alkyl groups comprising 3 to 10 carbon atoms; and unsubstituted or substituted aryl groups; and

wherein the at least one aldehyde compound according to Formula (I) has a concentration ranging from 0.01 to 25 mg/l.

In one embodiment \( R \) may be \(-\text{H}\). In another embodiment \( R \) is preferably not \(-\text{H}\).

In a preferred embodiment \( R \) is selected from the group consisting of \(-\text{H}\); unsubstituted or substituted, linear alkyl groups comprising 1 to 10 carbon atoms; and unsubstituted or substituted, branched alkyl groups comprising 3 to 10 carbon atoms.

In another preferred embodiment \( R \) is selected from the group consisting of unsubstituted or substituted, linear alkyl groups comprising 1 to 10 carbon at-
oms; and unsubstituted or substituted, branched alkyl groups comprising 3 to 10 carbon atoms.

In another preferred embodiment the unsubstituted or substituted, linear alkyl groups are preferably selected from unsubstituted or substituted, linear alkyl groups comprising 1 to 8 carbon atoms; more preferably 1 to 5 carbon atoms, even more preferably from 2 to 5 carbon atoms. Furthermore preferably, the unsubstituted or substituted, linear alkyl groups are selected from the group comprising n-pentyl group, n-butyl group, n-propyl group, ethyl group and methyl group; further more preferably from n-butyl group, n-propyl group, ethyl group, and methyl group; most preferably from n-butyl group, n-propyl group, and ethyl group.

In another embodiment the unsubstituted or substituted, branched alkyl groups are preferably selected from unsubstituted or substituted, branched alkyl groups comprising 3 to 8 carbon atoms; more preferably 3 to 5 carbon atoms. Even more preferably the unsubstituted or substituted, branched alkyl groups are selected from the group comprising 2-pentyl (sec-pentyl) group, 3-pentyl group, 2-methylbutyl group, 3-methylbutyl (iso-pentyl) group, 3-methylbut-2-yl group, 2-methylbut-2-yl group; 2,2-dimethylpropyl (neo-pentyl) group, iso-butyl group, sec-butyl group, tert-butyl group, and iso-propyl group; most preferably from iso-butyl group, sec-butyl group, and iso-propyl group.

In another embodiment the unsubstituted or substituted aryl groups are preferably selected from unsubstituted or substituted aryl groups comprising 6 to 10 carbon atoms; more preferably from unsubstituted or substituted phenyl groups and unsubstituted or substituted naphthyl groups; most preferably from unsubstituted or substituted phenyl groups.

In a further embodiment the linear alkyl groups, the branched alkyl groups, or the aryl groups are preferably substituted. Preferably, the substituents are se-
lected independently from each other from the group comprising amino, carbox-
yl, ester, mercapto, hydroxyl, methoxy, ethoxy, methyl, ethyl, halogen, such as
fluorine, chlorine, bromine, iodine; allyl, vinyl, and aryl groups; preferably from
amino, carboxyl, ester, hydroxyl, methoxy, ethoxy, methyl, ethyl, halogen, such
as fluorine, chlorine, bromine, iodine; and aryl groups; even more preferably
from carboxyl, ester, hydroxyl, methoxy, ethoxy, methyl, ethyl, halogen, such as
fluorine, chlorine, bromine, iodine; and aryl groups.

In a more preferred embodiment the at least one aldehyde compound according
to Formula (I) is selected from the group comprising hexanal (hexanaldehyde),
pentanal (valeraldehyde), butanal (butyraldehyde), propanal (propionaldehyde),
ethanal (acetaldehyde), methanal (formaldehyde), phenylmethanal (benzalde-
hyde), and 2-phenylacetaldheyde; preferably from n-hexanal, n-pentanal, n-
butanal, n-propanal, and ethanol; more preferably from n-pentanal, n-butanal, n-
propanal, and ethanol, even more preferably from n-hexanal, n-pentanal, n-
butanal, and n-propanal.

In so far as the term "alkyl" is used in this description and in the claims, it refers
to a hydrocarbon radical with the general chemical formula \( \text{C}_n\text{H}_{2n+1} \), \( n \) being an
integer from 1 to 10. Alkyl residues according to the present invention can be
linear and/or branched and they are preferably saturated. For example, linear
alkyl groups comprising 1 to 10 carbon atoms means linear alkyl groups having
a number of overall C atoms ranging from 1 to 10, respectively. Branched alkyl
groups comprising 3 to 10 carbon atoms means branched alkyl groups in which
the sum of C atoms in the main chain plus C atoms in the branching chains re-
sults in a number of overall C atoms ranging from 3 to 10, respectively. Linear
alkyl groups comprising 1 to 8 carbon atoms or branched alkyl groups comprising
3 to 8 carbon atoms for example include methyl, ethyl, propyl, butyl, pentyl,
hexyl, heptyl or octyl. Linear alkyl groups comprising 1 to 5 carbon atoms or
branched alkyl groups comprising 3 to 5 carbon atoms for example include me-
thyl, ethyl, propyl, butyl, or pentyl.
In so far as the term "aryl" is used in this description and in the claims, it refers to ring-shaped aromatic hydrocarbon radicals, for example phenyl or naphthyl.

Furthermore, alkyl and/or aryl can be substituted by replacing an H-atom in each case by a substituent as outlined above for the linear alkyl groups, the branched alkyl groups, and/or the aryl groups.

The at least one aldehyde compound according to Formula (I) has a concentration in the aqueous plating bath composition according to the present invention ranging from 0.01 to 25 mg/l; preferably from 0.01 to 10 mg/l, more preferably from 0.1 to 10 mg/l.

Surprisingly and in contrast to the prior art, it was found that aldehyde compounds increase the deposition rate of electroless palladium plating baths when contained therein in a concentration below the one used for aldehyde reducing agents.

The aqueous plating bath composition according to the present invention comprises at least one source for palladium ions. Preferably, the at least one source for palladium ions is a water soluble palladium compound. More preferably, the at least one source for palladium ions is selected from the group comprising palladium chloride, palladium acetate, palladium sulfate and palladium perchlorate. Optionally, complex compounds comprising a palladium ion and a complexing agent, preferably a nitrogenated complexing agent, for palladium ions can be added to the plating bath instead of forming such a complex compound in the plating bath by adding a palladium salt and said complexing agent for palladium ions to the plating bath as separate ingredients. Suitable complex compounds as sources for palladium ions are for example complex compounds comprising palladium ions and complexing agents; preferably nitrogenated complexing agents; more preferably ethane-1,2-diamine and/or alkyl substituted ethane-1,2-diamines. Suitable complex compounds may further comprise coun-
ter ions to palladium ions; preferably chloride, acetate, sulfate or perchlorate. Suitable nitrogenated complexing agents and alkyl substituted ethane-1,2-diamines are defined below as complexing agents. Preferably, suitable complex compounds as sources for palladium ions are for example dichloro ethane-1,2-diamine palladium diacetato ethane-1,2-diamine palladium; dichloro \( \text{N}^1 \)-methylethane-1,2-diamine palladium; diacetato \( \text{N}^1 \)-methylethane-1,2-diamine; dichloro \( \text{N}^1,\text{N}^2 \)-dimethylethane-1,2-diamine; diacetato \( \text{N}^1,\text{N}^2 \)-dimethylethane-1,2-diamine; dichloro \( \text{N}^1 \)-ethylethane-1,2-diamine; diacetato \( \text{N}^1 \)-ethylethane-1,2-diamine, dichloro \( \text{N}^1,\text{N}^2 \)-diethylethane-1,2-diamine; and diacetato \( \text{N}^1,\text{N}^2 \)-diethylethane-1,2-diamine.

The concentration of palladium ions in the composition ranges from 0.5 to 500 mmol/l, preferably from 1 to 100 mmol/l.

The aqueous plating bath composition according to the present invention further comprises at least one reducing agent for palladium ions. The reducing agent makes the plating bath an autocatalytic, i.e. an electroless plating bath. Palladium ions are reduced to metallic palladium in the presence of said reducing agent. This plating mechanism differentiates the plating bath according to the present invention from 1) immersion-type palladium plating baths which do not contain a reducing agent for palladium ions and 2) plating baths for electroplating of palladium which require an external electrical current in order to deposit a palladium layer.

The at least one reducing agent is preferably a chemical reducing agent. Reducing agents provide the electrons necessary to reduce metal ions to their metallic form and thereby form a metal deposit on a substrate.

More preferably, the at least one reducing agent is a reducing agent for depositing pure palladium deposits. Pure palladium deposits are deposits containing
palladium in an amount ranging from 98.0 to 99.99 wt.-% or higher, preferably from 99.0 to 99.99 wt.-% or higher.

Even more preferably, the at least one reducing agent for palladium ions is selected from the group consisting of hydrazine, formic acid, derivatives of the aforementioned and salts thereof.

Yet even more preferably, the at least one reducing agent for palladium ions is selected from the group consisting of formic acid, derivatives of formic acid and salts of the aforementioned. Yet even more preferably, the formic acid derivatives are selected from esters of formic acid. Yet even more preferably, esters of formic acid are selected from the group consisting of formic acid methylester, formic acid ethylester and formic acid propylester. Suitable counter ions for salts of formic acid are for example selected from hydrogen, lithium, sodium, potassium and ammonium. The aqueous plating bath composition according to the present invention is particularly suitable for depositing palladium layers in the presence of formic acid, derivatives and salts of the aforementioned as reducing agent.

Preferably, the at least one reducing agent is not formaldehyde.

Preferably, the concentration of the at least one reducing agent in the aqueous plating bath composition according to the present invention ranges from 10 to 1000 mmol/l.

Preferably, the molar ratio of the reducing agent for palladium ions and the palladium ions in the composition according to the present invention ranges from 1 : 10 to 10 : 1; more preferably from 1 : 5 to 5 : 1; even more preferably from 1 : 3 to 3 : 1.

The aqueous plating bath composition of the present invention is particularly suitable for depositing pure palladium layers. Pure palladium layers are particu-
larly suitable for high temperature applications like in motor control units as pure palladium layers allow for sufficient thermal stability of bonded or soldered connections.

Hypophosphite ions and/or amine borane compounds and/or sodium borhydride are not suitable as the reducing agent because palladium alloy layers are deposited from such plating bath compositions.

The aqueous plating bath composition according to the present invention may further comprise at least one complexing agent for palladium ions. A complexing agent (sometimes also referred to as chelating agent) keeps metal ions dissolved and prevents their undesired precipitation from solution.

Preferably, the at least one complexing agent is a nitrogenated complexing agent for palladium ions. More preferably, the at least one nitrogenated complexing agent is selected from the group comprising primary amines, secondary amines and tertiary amines. Even more preferably, the at least one nitrogenated complexing agent is selected from the group comprising diamines, triamines, tetraamines and higher homologues thereof.

Suitable amines are for example ethane-1,2-diamine (NH₂-CH₂-CH₂-NH₂, ethylene diamine); alkyl substituted ethane-1,2-diamines; 1,3-diamino-propane; 1,2-bis (3-amino-propyl-amino)-ethene; diethylene-triamine; diethylene-triamine-penta-acetic acid; N-(2-hydroxy-ethyl)-ethylene-diamine; ethylene-diamine-N,N-diacetic acid; 1,2-diamino-propyl-amine; 1,3-diamino-propyl-amine; 3-(methyl-amino)-propyl-amine; 3-(dimethyl-amino)-propyl-amine; 3-(diethyl-amino)-propyl-amine; bis-(3-amino-propyl)-amine; 1,2-bis-(3-amino-propyl)-alkyl-amine; diethylene-triamine; triethylene-tetramine; tetra-ethylene-pentamine; penta-ethylene-hexamine and mixtures thereof.

Suitable alkyl substituted ethane-1,2-diamines are for example N¹-methylethane-1,2-diamine (CH₃-NH-CH₂-CH₂-NH₂); N¹,N²-dimethylethane-1,2-
diamine \((\text{CH}_3-\text{NH-CH}_2-\text{CH}_2-\text{NH-CH}_3)\); \(\text{N}^1,\text{N}^1\)-dimethylene-1,2-diamine \(((\text{CH}_3)_2\text{-N-CH}_2\text{-CH}_2\text{-NH}_2)\); \(\text{N}^1,\text{N}^1,\text{N}^2\)-trimethylene-1,2-diamine \(((\text{CH}_3)_2\text{-N-CH}_2\text{-CH}_2\text{-NH-CH}_3)\); \(\text{N}^1,\text{N}^1,\text{N}^2,\text{N}^2\)-tetramethylene-1,2-diamine \(((\text{CH}_3)_2\text{-N-CH}_2\text{-CH}_2\text{-N-(CH}_3)_2)\); \(\text{N}^1\)-ethylenethane-1,2-diamine \((\text{C}_2\text{H}_5\text{-NH-CH}_2\text{-CH}_2\text{-NH}_2)\); \(\text{N}^1,\text{N}^2\)-diethylethane-1,2-diamine \((\text{C}_2\text{H}_5\text{-NH-CH}_2\text{-CH}_2\text{-NH-C}_2\text{H}_5)\); \(\text{N}^1\)-ethyl-N\(^2\)-methylene-1,2-diamine \((\text{C}_2\text{H}_5\text{-NH-CH}_2\text{-CH}_2\text{-NH-CH}_3)\); \(\text{N}^1\)-ethyl-N\(^1\)-methylene-1,2-diamine \(((\text{CH}_3)\text{(C}_2\text{H}_3)\text{-N-CH}_2\text{-CH}_2\text{-NH}_2)\); \(\text{N}^1,\text{N}^1\)-diethylethane-1,2-diamine \(((\text{CH}_3)\text{(C}_2\text{H}_3)\text{-N-CH}_2\text{-CH}_2\text{-NH-CH}_3)\); \(\text{N}^1,\text{N}^1,\text{N}^2\)-diethylethane-1,2-diamine \(((\text{CH}_3)\text{(C}_2\text{H}_5)\text{-N-CH}_2\text{-CH}_2\text{-NH-(C}_2\text{H}_5))\); \(\text{N}^1,\text{N}^1\)-diethyl-N\(^2\)-methylene-1,2-diamine \(((\text{C}_2\text{H}_5)\text{-N-CH}_2\text{-CH}_2\text{-NH-CH}_3)\); \(\text{N}^1,\text{N}^1,\text{N}^2\)-triethylethane-1,2-diamine \(((\text{C}_2\text{H}_5)\text{-N-CH}_2\text{-CH}_2\text{-NH-C}_2\text{H}_5)\); \(\text{N}^1\)-ethyl-N\(^1\),\text{N}^2\)-trimethylene-1,2-diamine \(((\text{CH}_3)\text{(C}_2\text{H}_5)\text{-N-CH}_2\text{-CH}_2\text{-N-(CH}_3\text{)}_2)\); \(\text{N}^1,\text{N}^2\)-diethyl-N\(^1\),\text{N}^2\)-dimethylene-1,2-diamine \(((\text{CH}_3)\text{(C}_2\text{H}_3)\text{-N-CH}_2\text{-CH}_2\text{-N-(CH}_3\text{)}\text{(C}_2\text{H}_3))\); \(\text{N}^1,\text{N}^1\)-diethyl-N\(^2\),\text{N}^2\)-dimethylene-1,2-diamine \(((\text{C}_2\text{H}_5)\text{-N-CH}_2\text{-CH}_2\text{-N-(CH}_3\text{)}_2)\); \(\text{N}^1,\text{N}^1,\text{N}^2\)-triethyl-N\(^2\)-methylene-1,2-diamine \(((\text{C}_2\text{H}_5)\text{-N-CH}_2\text{-CH}_2\text{-N-(CH}_3\text{)}\text{(C}_2\text{H}_3))\); \(\text{N}^1,\text{N}^1,\text{N}^2,\text{N}^2\)-tetraethylethane-1,2-diamine \(((\text{C}_2\text{H}_5)\text{-N-CH}_2\text{-CH}_2\text{-N-(C}_2\text{H}_3)_2)\) and mixtures thereof.

Preferably, the mole ratio of the complexing agent for palladium ions and palladium ions in the composition according to the present invention ranges from 1 : 1 to 50 : 1.

The aqueous plating bath composition according to the present invention may further comprise at least one stabilizing agent. Stabilizing agents, also referred to as stabilizers, are compounds that stabilize an electroless metal plating solution against undesired outplating in the bulk solution and spontaneous decomposition. The term "outplating" means undesired and/or uncontrolled deposition of the metal on surfaces other than substrate surfaces.
The at least one stabilizing agent may be selected from the group comprising compounds of the elements selenium, tellurium, copper, nickel, and iron and/or mercapto-benzothiazole, seleno-cyanates, thiourea, saccharin, ferro-cyanates; 4-nitrobenzoic acid; 3,5-dinitrobenzoic acid; 2,4-dinitrobenzoic acid; 2-hydroxy-3,5-dinitrobenzoic acid; 2-acetylbenzoic acid; 4-nitrophenol and their corresponding ammonium, sodium and potassium salts.

Preferably, the concentration of such further stabilizing agents in the composition according to the present invention ranges from 0.01 to 500 mg/l, more preferably from 0.1 to 200 mg/l, even more preferably from 1 to 200 mg/l, and most preferably from 10 to 100 mg/l.

Preferably, the aqueous plating bath composition according to the present invention is an acidic plating bath. The pH-value of the aqueous plating bath composition more preferably ranges from 4 to 7 because the composition is unstable at a pH-value below 4. Even more preferably, the pH-value of the composition ranges from 5 to 6. At pH-values above 7, the composition is prone to deposit palladium onto the substrate by immersion-type plating resulting in a weak adhesion between the palladium layer and the subjacent substrate. Furthermore, a plating bath composition having a pH-value above 7 would attack organic resist materials such as solder mask materials which may also be a part of the substrate.

The present invention further relates to a method for electroless palladium plating comprising the steps of
  a) providing a substrate,
  b) contacting the substrate with the aqueous plating bath composition according to the present invention and thereby depositing a layer of palladium onto at least a portion of the substrate.
Preferably, the method steps are performed in the order described above. Preferably, the substrate has a metal surface.

Palladium plating or deposition of palladium is preferably carried out by contacting a substrate having a metal surface with the composition according to the present invention and thereby depositing a layer of palladium onto at least a portion of the metal surface of the substrate. Preferably, the metal surface or the portion thereof to be coated with palladium is selected from the group comprising copper, copper alloys, nickel, nickel alloys, cobalt, cobalt alloys, platinum, platinum alloys, gold, gold alloys, and gallium arsenide. The metal surface or the portion thereof to be coated is for example part of a printed circuit board, an IC substrate or a semiconducting wafer. Palladium layers are used for example on semiconducting wafers as noble metal, wire-bondable and solderable finishes of semiconductor chips, light emitting diodes (LED) or solar cells.

Suitable methods for contacting the substrate with the aqueous plating bath composition are for example dipping the substrate into the composition or spraying the composition onto the substrate.

Preferably, the substrate is contacted with the aqueous plating bath composition according to step b) at a temperature of 30 to 95°C, more preferably of 30 to 85°C, even more preferably of 50 to 85°C, yet even more preferably of 30 to 65°C. Preferably, the substrate is contacted with the composition for 1 to 60 min, more preferably 10 to 20 min. Preferably, the substrate is contacted with the aqueous plating bath composition to give a palladium plated layer ranging in thickness from 0.01 to 5.0 μηι, more preferably from 0.02 to 2.0 μηι and even more preferably from 0.05 to 0.5 μηι.

The thickness of palladium layers was measured by x-ray fluorescence (XRF) which is well known to persons skilled in the art. The XRF measurements make use of the characteristic fluorescence radiation emitted from a sample (sub-
strate, deposit) being excited with x-rays. By evaluating the wavelength and intensities and assuming a layered structure of the sample, layer thicknesses can be calculated.

In one embodiment of the present invention, a thin activation layer of palladium is first deposited onto the substrate, preferably a substrate having a metal surface, by an immersion-type plating method (exchange reaction) followed by palladium deposition from the aqueous plating bath composition according to the present invention.

Activation methods for the metal surface prior to electroless palladium deposition are known in the art and can be applied to work within the present invention. A suitable aqueous activation bath may comprise a palladium salt such as palladium acetate, palladium sulfate and palladium nitrate, a complexing agent for palladium ions such as primary amines, secondary amines, tertiary amines and ethanolamines and an acid such as nitric acid, sulfuric acid and methane sulfonic acid. Optionally, such an activation bath further contains an oxidizing agent such as nitrate ions, perchlorate ions, chlorate ions, perborate ions, periodate ions, peroxo-disulfate ions and peroxide ions.

The concentration of the palladium salt in the aqueous activation bath ranges from 0.005 to 20 g/l, preferably from 0.05 to 2.0 g/l. The concentration of the complexing agent for palladium ions ranges from 0.01 to 80 g/l, preferably from 0.1 to 8 g/l.

The pH-value of the aqueous activation bath preferably ranges from 0 to 5, preferably from 1 to 4.

Typically, the substrates are immersed in the aqueous activation bath at 25 to 30°C for one to four minutes. Prior to immersing the substrate in an aqueous activation bath, the metal surface of the substrate is cleaned. For this purpose, etch cleaning is usually carried out in oxidizing, acidic solutions, for example a
solution of sulfuric acid and hydrogen peroxide. Preferably, this is followed by another cleaning in an acidic solution, such as, for example, a sulfuric acid solution.

The aldehyde compounds according to Formula (I) of the present invention increase the deposition rate of aqueous plating bath compositions for electroless deposition of palladium, in particular for electroless deposition of pure palladium. Thus, the aqueous plating bath compositions are activated and the deposition process is accelerated. This contributes to acceleration of the manufacturing process.

The deposition rate of known electroless palladium deposition baths usually constantly decreases during bath life. Thus, a longer plating time is required to obtain palladium layers of the same thickness and quality when plating with an aged palladium deposition bath compared to a freshly prepared palladium deposition bath. Adding the aldehyde compounds according to Formula (I) to an electroless palladium plating bath allows for adjusting the deposition rate to a constant range over the bath life time, in particular to a constant high range of deposition rate over the bath life. This ensures depositing palladium layers of constant thickness throughout the life time of an electroless palladium plating bath and facilitates process control of the manufacturing process.

If the deposition rate of known electroless palladium deposition baths becomes too low the deposition bath is no more suited for depositing palladium and has to be discarded. Adjusting the deposition rate to a constant range over the bath life time, in particular to a constant high range, also prolongs the life time of an electroless palladium plating bath.

In addition, the aldehyde compounds according to Formula (I) of the present invention activate electroless palladium plating baths having a low deposition rate even when freshly prepared. Further, the aldehyde compounds according
to Formula (I) of the present invention reactivate aged electroless palladium plating baths. Aged electroless palladium plating bath means herein an electroless palladium plating bath already used for plating and whose deposition rate already dropped during such usage. Reactivating means herein that the aldehyde compounds according to Formula (I) also increase the deposition rate of an aged electroless palladium plating bath.

For known electroless palladium plating baths and deposition methods, regulating the deposition rate and duration of bath life is achieved by increasing the bath temperature to between 55 to 95°C during deposition. But a raised temperature of the electroless palladium plating baths has several disadvantages. Operating the bath at a higher temperature increases the risk of destabilising the bath. It requires higher energy consumption. It is of disadvantage for layers of some metals also present on the substrate to be plated. For example, aluminium or copper layers suffer corrosion when present on a substrate which is plated with palladium from a deposition bath at higher temperatures. The aldehyde compounds according to Formula (I) of the present invention allow for electrolessly depositing palladium layers at lower temperatures ranging from 30 to 65 °C. Thus, stability of the aqueous plating bath compositions of the present invention is maintained and corrosion of metal layers also present on the substrate during deposition of palladium from the composition is prevented.

The present invention further relates to a method for adjusting the deposition rate to a constant range over the life time of any electroless palladium deposition bath, the method comprises the steps of

c) providing any electroless palladium deposition bath, and

d) adding at least one aldehyde compound according to Formula (I) as defined above to the electroless palladium deposition bath.
The electroless palladium deposition bath may be any electroless palladium deposition bath, e.g. any aqueous electroless palladium deposition bath. In one embodiment the electroless palladium deposition bath is the aqueous plating bath composition according to the present invention.

In one embodiment of the present invention the electroless palladium deposition bath may be a freshly prepared electroless palladium deposition bath.

In another embodiment the electroless palladium deposition bath may be already used for some time for plating.

Further, in a preferred embodiment, the electroless palladium deposition bath is a bath for electroless deposition of pure palladium.

The deposition rate or the concentration of the at least one aldehyde compound according to Formula (I) may be determined during plating or storage. If the deposition rate or the concentration of the at least one aldehyde compound according to Formula (I) are below a threshold value, the at least one aldehyde compound according to Formula (I) is replenished. Replenishment is performed by adding the at least one aldehyde compound according to Formula (I) to the electroless palladium deposition baths.

The at least one aldehyde compound according to Formula (I) may be added as a solid or a powder or may be dissolved in a solvent prior to its addition to the electroless palladium deposition baths. Examples for suitable solvents are water; acids like sulphuric acid, hydrochloric acid, phosphoric acid; alkaline solutions like solutions of sodium hydroxide or potassium hydroxide; and organic solvents like propanol, ethanol, methanol.

In another preferred embodiment the electroless palladium deposition bath may be already used for some time for plating and the deposition rate has dropped in relation to the initial deposition rate. In this embodiment, the present invention
relates to a method for reactivating the aqueous electroless palladium deposition bath, the method comprises the steps of

e) providing an already used aqueous electroless palladium deposition bath, wherein its deposition rate has dropped in relation to its initial deposition rate, and

f) adding at least one aldehyde compound according to Formula (I) as defined above, and thereby increasing its deposition rate.

The present invention further relates to uses of the aldehyde compounds according to Formula (I) for

accelerating palladium deposition from any electroless palladium deposition bath, and/or

adjusting the deposition rate to a constant range over the life time of any electroless palladium deposition bath, and/or

reactivating an electroless palladium deposition bath already used for plating, wherein its deposition rate has dropped in relation to its initial deposition rate.
Examples

The present invention is further explained by the following non-limiting examples.

General procedures

Substrates and pre-treatment:
Test chips made of silicon covered with a SiO₂ layer and having four dies each were used as substrates. Each die had several isolated pads of an aluminum-copper alloy on its surface. The pads had different sizes ranging from 10 µm to 1000 µm in diameter and distances between pads ranged from 20 µm to 1000 µm.

The test chips were already pre-treated by double-zincation. Afterwards, the test chips were nickel plated using an electroless nickel plating bath (Xenolyte Ni MP, product of Atotech Deutschland GmbH) containing a nickel(II) salt, a reducing agent for nickel ions, a complexing agent for nickel ions and a stabilizer. The nickel plating bath had a pH value of 4.5 and was held at 87 °C during plating. The test chips were immersed into the nickel plating bath for 10 minutes and a nickel layer of 3 µm thickness was plated onto the test chips. Afterwards, the test chips were rinsed in deionized water and subjected to a palladium plating bath.

Palladium plating bath matrix and palladium plating:
A plating bath matrix (Xenolyte Pd LL, product of Atotech Deutschland GmbH) having a pH-value of 5.5 and comprising water, palladium ions, sodium formate as reducing agent for palladium ions and ethylene diamine as complexing agent for palladium ions was used throughout all examples. Sodium formate of different manufacturing batches having different purities was used in the examples.
Different amounts of the aldehyde compounds according to Formula (I) of the present invention were added to 2 l of individual palladium plating bath matrices throughout examples 1 to 4. The aqueous plating bath compositions were held at 55 °C during plating. The substrates were immersed into the aqueous plating bath compositions for 6 minutes. Afterwards, the substrates were rinsed with deionized water for 1 minute and dried with air pressure.

Determining the deposition rate:
The thickness of the palladium layers deposited in various aqueous plating bath compositions tested was determined with an X-ray fluorescence method (XRF; Fischer, Fischerscope® X-Ray XDV®-1). The thickness was measured on four palladium pads for each substrate. The deposition rate for each aqueous plating bath composition was calculated by dividing the measured thickness of the palladium layers deposited by the plating time of 6 minutes. The mean values of deposition rates for each substrate are presented in Examples 1 to 4 below.

Example 1
Example 1 was performed with plating bath matrices containing different batches of sodium formate, namely batch 2 having high purity and batch 3 having lower purity. 0 to 10 mg/l of formaldehyde were added to the plating bath matrices. The aqueous plating bath compositions and plating results are summarised in Table 1 and shown in Figure 1.

Table 1: Deposition rate of aqueous plating bath compositions containing formaldehyde

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<th>Concentration of formaldehyde [mg/l]</th>
<th>Deposition rate [nm/min]</th>
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<td></td>
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</table>
Example 2

Example 2 was performed with plating bath matrices containing different batches of sodium formate, namely batch 2 having high purity and batch 3 having lower purity. 0 to 10 mg/l of n-propanal were added to the plating bath matrices. The aqueous plating bath compositions and plating results are summarised in Table 2 and shown in Figure 2.

Table 2: Deposition rate of aqueous plating bath compositions containing n-propanal

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<tr>
<th></th>
<th>Concentration of n-propanal [mg/l]</th>
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<tr>
<td>invention</td>
<td>10</td>
<td>65</td>
</tr>
</tbody>
</table>

Example 3

0 to 1.25 mg/l of n-pentanal were added to the plating bath matrix. The plating bath matrix contained sodium formate of manufacturing batch 1 having highest purity. The aqueous plating bath compositions and plating results are summarised in Table 3 and shown in Figure 3.

Table 3: Deposition rate of aqueous plating bath compositions containing n-pentanal

<table>
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<tr>
<th></th>
<th>Concentration of n-pentanal [mg/l]</th>
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</table>
Example 4

0 to 10 mg/l of n-pentanal were added to the plating bath matrix. The plating bath matrix contained sodium formate of manufacturing batch 2 having high purity. The aqueous plating bath compositions and plating results are summarised in Table 4 and shown in Figure 4.

Table 4: Deposition rate of aqueous plating bath compositions containing n-pentanal

<table>
<thead>
<tr>
<th></th>
<th>Concentration of n-pentanal [mg/l]</th>
<th>Deposition rate [nm/min] reducer of batch 2</th>
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<td>58</td>
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</table>

Summary of Results of Examples 1 to 4

Examples 1 to 4 showed that the deposition rate of aqueous plating bath compositions containing aldehyde compounds according to Formula (I) were higher compared to compositions lacking the aldehyde compounds. The deposition rate increased with increasing concentration of the aldehyde compounds. The deposition rates for compositions having no aldehyde compounds contained therein (comparative compositions of Examples 1 to 4) differ from each other due to the different batches of sodium formate used therein.

The deposits obtained from aqueous plating bath compositions with or without aldehyde compounds according to Formula (I) had a purity of between 98 to 99.99 wt.-%, were ductile, had a grey to white colour and adhered very well to the substrates.

Example 5
0 to 50 mg/l of n-pentanal were added to the plating bath matrix. The plating bath matrix contained sodium formate of manufacturing batch 2 having high purity. The aqueous plating bath compositions and plating results are summarised in Table 5.

Table 5: Deposition rate of aqueous plating bath compositions containing n-pentanal

<table>
<thead>
<tr>
<th>Concentration of n-pentanal [mg/l]</th>
<th>Deposition rate [nm/min] reducer of batch 2</th>
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<td></td>
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<td>50</td>
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</table>

Example 6
0 to 1.25 mg/l of n-hexanal were added to the plating bath matrix. The plating bath matrix contained sodium formate of manufacturing batch 1 having highest purity. The aqueous plating bath compositions and plating results are summarised in Table 6.

Table 6: Deposition rate of aqueous plating bath compositions containing n-pentanal

<table>
<thead>
<tr>
<th>Concentration of n-pentanal [mg/l]</th>
<th>Deposition rate [nm/min] reducer of batch 1</th>
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<tr>
<td>comparative</td>
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<td>according to invention</td>
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</table>


**C L A I M S**

1. An aqueous plating bath composition for electroless deposition of palladium, comprising
   (i) at least one source for palladium ions,
   (ii) at least one reducing agent for palladium ions, and
   (iii) at least one aldehyde compound according to Formula (I)

   \[
   \text{R-C-H}
   \]  
   Formula (I),

   wherein \( R \) is selected from the group consisting of -H; unsubstituted or
   substituted, linear alkyl groups comprising 1 to 10 carbon atoms; and
   unsubstituted or substituted, branched alkyl groups comprising 3 to
   10 carbon atoms; and substituted or unsubstituted aryl groups; and

   wherein the at least one aldehyde compound according to Formula (I) has
   a concentration ranging from 0.01 to 25 mg/l.

2. The aqueous plating bath composition according to claim 1, wherein the
   unsubstituted or substituted, linear alkyl groups are selected from the
   group comprising n-pentyl group, n-butyl group, n-propyl group, ethyl
   group and methyl group.

3. The aqueous plating bath composition according to claim 1, wherein the
   unsubstituted or substituted, branched alkyl groups are selected from the
   group comprising 2-pentyl group, 3-pentyl group, 2-methylbutyl group, 3-
   methylbutyl group, 3-methylbut-2-yl group, 2-methylbut-2-yl group; 2,2-
   dimethylpropyl group, iso-butyl group, sec-butyl group, tert-butyl group,
   and iso-propyl group.
4. The aqueous plating bath composition according to claim 1, wherein the unsubstituted or substituted aryl groups are selected from unsubstituted or substituted phenyl groups and unsubstituted or substituted naphthyl groups.

5. The aqueous plating bath composition according to any of the foregoing claims, wherein the linear alkyl groups, the branched alkyl groups, or the aryl groups are substituted and the substituents are selected independently from each other from the group comprising amino, carboxyl, ester, mercapto, hydroxyl, methoxy, ethoxy, methyl, ethyl, halogen, allyl, vinyl, and aryl groups.

6. The aqueous plating bath composition according to any of the foregoing claims, wherein the at least one aldehyde compound according to Formula (I) is selected from hexanal, pentanal, butanal, propanal, ethanal, methanal, phenylmethanal, and 2-phenylacetaldehyde.

7. The aqueous plating bath composition according to any of the foregoing claims, wherein the at least one source for palladium ions is selected from the group comprising palladium chloride, palladium acetate, palladium sulfate, palladium perchlorate, dichloro ethane-1,2-diamine palladium, diacetato ethane-1,2-diamine palladium; dichloro N\textsuperscript{1}-methylethene-1,2-diamine palladium; diacetato N\textsuperscript{1}-methylethene-1,2-diamine; dichloro N\textsuperscript{1},N\textsuperscript{2}-dimethylethene-1,2-diamine; diacetato N\textsuperscript{1},N\textsuperscript{2}-dimethylethene-1,2-diamine; dichloro N\textsuperscript{1}-ethylethene-1,2-diamine; diacetato N\textsuperscript{1}-ethylethene-1,2-diamine; dichloro N\textsuperscript{1},N\textsuperscript{2}-diethylethene-1,2-diamine; and diacetato N\textsuperscript{1},N\textsuperscript{2}-diethylethene-1,2-diamine.

8. The aqueous plating bath composition according to any of the foregoing claims, further comprising at least one complexing agent for palladium
ions selected from the group consisting of primary amines, secondary amines and tertiary amines.

9. The aqueous plating bath composition according to any of the foregoing claims, wherein the at least one reducing agent for palladium ions is selected from the group consisting of hydrazine, formic acid, derivatives of the aforementioned and salts thereof.

10. The aqueous plating bath composition according to claim 9, wherein the formic acid derivatives are selected from esters of formic acid.

11. The aqueous plating bath composition according to any of the foregoing claims, wherein the concentration of the at least one reducing agent ranges from 10 to 1000 mmol/l.

12. A method for electroless palladium plating comprising the steps of
   (a) providing a substrate,
   (b) contacting the substrate with the aqueous plating bath composition according to any of claims 1 to 12 and thereby depositing a layer of palladium onto at least a portion of the substrate.

13. The method for electroless palladium plating according to claim 12 wherein the substrate is contacted with the aqueous plating bath composition at a temperature of 30 to 65°C in step (b).

14. A method for adjusting the deposition rate to a constant range over the lifetime of any electroless palladium deposition bath, the method comprises the steps of
   c) providing any electroless palladium deposition bath, and
   d) adding at least one aldehyde compound according to Formula (I) as defined by claim 1 to the electroless palladium deposition bath.
15. A method for reactivating an aqueous electroless palladium deposition bath, the method comprises the steps of

e) providing an already used aqueous electroless palladium deposition bath, wherein its deposition rate has dropped in relation to its initial deposition rate, and

f) adding at least one aldehyde compound according to Formula (I) as defined by claim 1, and thereby increasing its deposition rate.
### INTERNATIONAL SEARCH REPORT

**A. CLASSIFICATION OF SUBJECT MATTER**

INV. C23C18/44

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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Further documents are listed in the continuation of Box C.

**Date of the actual completion of the international search**

24 March 2016

**Date of mailing of the international search report**

08/04/2016

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk
Tel.: (+31-70) 340-2040, Fax: (+31-70) 340-3016

Authorized officer

Telias, Gabriela
## DOCUMENTS CONSIDERED TO BE RELEVANT

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