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(71) Applicant: **INTERUNIVERSITAIR
MICRO-ELEKTRONICA CENTRUM VZW
3001 Heverlee (BE)**

(72) Inventor: **Palmans, Roger
3770 Riemst (BE)**

(74) Representative: **Van Malderen, Joelle et al
Office Van Malderen,
Place Reine Fabiola 6/1
1083 Bruxelles (BE)**

(54) Method for depositing copper or a copper alloy on an aluminium containing substrate

(57) Method for depositing copper or copper alloy on a second metal substrate, made of aluminum or containing aluminum alloys, comprising the steps of :

- preparing a solution containing a source of copper Cu(II) ions, a complexing agent for said Cu(II) ions and an additive to adjust the pH of the solution to a required value;
- immersing said metal substrate in said solution for a predetermined period whereby growing a copper layer on said second metal substrate.

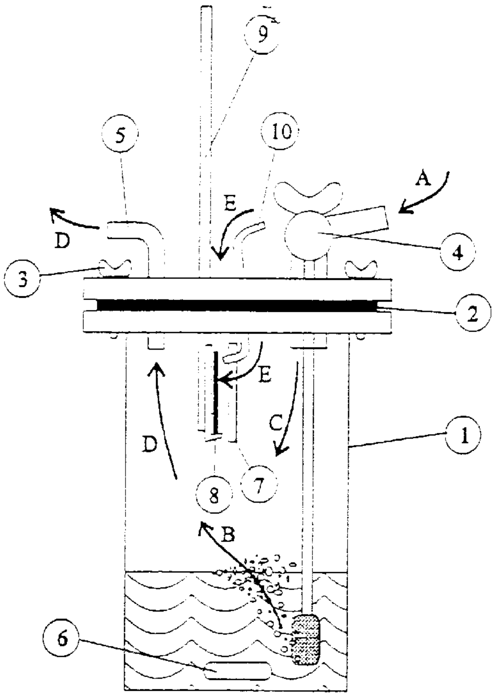

Fig. 1

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Description

Object of the invention

The present invention is related to a method for depositing a copper or a copper alloy on a second metal substrate, made of aluminum or of an aluminum alloy such as Al(Si) or Al(Cu) or Al(Si, Cu) or any similar alloy.

The present invention is also related to applications making use of this method.

State of the Art

Electroless deposition of metals on substrates made of aluminum or of aluminum alloys has always been hampered by the susceptibility of aluminum to dissolution in the deposition baths due to the aggressive nature of these solutions. Usually, this results in an imperfect adhesion between the metal coating and the aluminum substrate. Complete and reliable coverage of a substrate made of aluminum alloys with a metal requires that the native Al_2O_3 layer is removed, and that the subsequent reoxidation of the Al surface has to be avoided when the substrate is transferred to the metal deposition bath.

Another recurrent problem is the formation of an insulating Al_2O_3 layer on the aluminum substrate during metal deposition, such as the one observed during autocatalytic electroless copper deposition in an alkaline formaldehyde bath. Such bath typically contains a source of Cu(II)ions, a complexing ligand for Cu(II) ions, formaldehyde as a sacrificial reductant as well as sodium hyroxide to adjust the pH of the solution to the level required for formaldehyde to work as electron donor (see document JP-A-2310375 of Toshiba Corp.)

Specifically, when a copper film is to be plated on thin aluminum films in the fabrication process of VLSI electronic circuits, the dissolution of the aluminum in the copper deposition bath is a critical item. Aluminum films or Al(Si) or Al(Si, Cu) films as thin as 200 nm have to be treated for VLSI applications.

The state-of-the-art fails to disclose a method for depositing Cu on thin films of Al using a simple and cheap process and such that no degradation of the Al thin film occurs.

A classical solution to the problem of depositing a metal on an aluminum substrate is the application of a zincate treatment prior to metal deposition. During zincate treatment, aluminum present on the surface of the substrate is displaced by Zn which protects the substrate surface against reoxidation. In the subsequent electroless metal bath, the Zn coating is redissolved and another metal can be deposited on the oxide-free aluminum substrate. However, the substrate has to be prepared in order to yield a uniform Zn deposit before the zincate treatment can be applied. This procedure involves first an alkaline cleaning of the substrate, and secondly a conditioning of the Al substrate in a concentrated nitric acid solution (50 % by volume) which imparts a uniform thin Al_2O_3 coating on the aluminum substrate and removes alloying elements from the surface. Standardized processing with this technology however has proven to be difficult.

Document US-A-4400415 describes a process for electroless deposition of a coating of nickel on an aluminum or aluminum alloy substrate. The process comprises the steps of immersing the substrate in a hydroxide solution and electrolytically or electrolessly coating a layer of nickel thereon. The solution has a pH of about 12 or above, a nickel or cobalt compound soluble therein and a non-cyanide complexing agent for the nickel or cobalt compound capable of maintaining the nickel or cobalt metal in solution at a pH of about 12 or above. However, in using a solution with a pH of 12 or above, the aluminum or aluminum alloy substrate is expected to be attacked or degraded substantially.

Aims of the present invention

The aim of the present invention is to disclose a method which yields in a reproducible way immersion metal deposition on a second metal substrate made of aluminum or of an aluminum alloy.

The process can be used for further electroless metal plating (e.g. with Ni/Au), and is much simpler and cheaper compared to the methods as described in the state of the art.

Another aim of the present invention is to suggest an immersion metal deposition method on an aluminum substrate which does not require any cleaning or conditioning of the substrate surface prior to the deposition in contrast to zincate processing.

A further aim of the present invention is to suggest a method which will result in immersion plated metal layers which show good uniformity and good adhesion to the aluminum substrate even without a subsequent thermal treatment.

Main characteristics of the present invention

The present invention is related to a method for depositing copper or copper alloy on a second metal substrate, made of aluminum or containing aluminum alloys, comprising the steps of :

- preparing a solution containing a source of Cu(II) ions, a complexing agent for said Cu(II) ions and an additive to adjust the pH of the solution to a required value;
- immersing said metal substrate in said solution for a predetermined period whereby growing a copper layer on said second metal substrate.

Said solution is preferably an aqueous solution and does not contain a reductant such as formaldehyde.

The additive to adjust the pH of the solution is preferably sodium hydroxide.

Preferably, the pH adjusted to a value comprised between 10.0 and 11.5 and more particularly between 10.2 and 11.0.

The deposition of the copper or copper alloy on the second metal substrate can be achieved by immersing said substrate in a single solution.

According to one preferred embodiment, the method further comprises the step of:

- removing the oxygen from said solution through bubbling an inert gas through said solution and
- immersing thereafter the aluminum substrate in the solution while keeping said solution under an inert gas atmosphere during the copper deposition.

Preferably the inert gas is Argon or Nitrogen.

According to another preferred embodiment, the method further comprises the step of:

- depositing a further metal layer such as Ni or Ni followed by Au after the deposition of the copper or copper alloy.

The ratio of the concentrations of tartrate/Cu(II) should be higher than 2 and preferably around 4.6.

More specifically, the concentration of Cu(II) ions in the solution is comprised in the range of 0.7^{10-2} - 7.2^{10-2} molar.

The Al alloy is Al(Si), Al(Cu), Al(Si, Cu) wherein the percentage of Si and/or Cu does not exceed 2%.

The present invention is also related to specific applications of the method of the invention such as selective deposition or flip-chip applications.

Brief description of the drawing

Figure 1 represents a schematic view of a device used for achieving the method of the present invention according to one preferred embodiment.

Detailed description of preferred embodiments of the present invention

Figure 1 schematically represents a device which permits to achieve the method of the present invention.

The device consists of a reaction vessel (1) having a rubber-O ring (2) to seal the lid by means of safety bolts (3).

A 3-way valve diffuser (4) is also provided in order to let the inert gas such as N_2 to bubble through the solution present in the reaction vessel (1) with the aim of deoxygenating the solution prior to the metal deposition. In the solution, a magnetic stirrer (6) is provided in order to have a good diffusion of the inert gas into the solution. The flow path of the inert gas is symbolized by arrows A, B, C, D while the arrow E represents the rinsing water going through the rinsing nozzle (10) used after plating.

A substrate or wafer (8) is fixed on a wafer support (9) and is covered by a protection plate (7). The substrate is immersed in the solution after the solution is deoxygenated (typically after 10-20 minutes). The copper deposition preferably is to performed while the solution is kept under an inert atmosphere (nitrogen or argon) in order to avoid in situ oxidation of the copper layer during deposition in the bath.

To this end, the deposition can be performed in a glass reactor as shown in figure 1 for a period of 10 to 20 minutes with nitrogen purge of the deposition solution before the substrate is immersed in the bath. During the deposition step the flow of nitrogen is maintained over the solution. Stirring of the solution is not necessary but can be applied. Stirring results in the deposition of a slightly thicker copper layer. After the required deposition time in the copper deposition bath, the wafer is rinsed with deionized water and can be either dried in a gas flow or used as such for further processing such as a nickel deposition.

A preferred embodiment is hereunder described with reference to a substrate made of an Al(1% Si) alloy.

By using the device as described in figure 1, a thin uniform film of copper can be deposited on the substrate made of Al(1% Si) alloy. This is deposited by immersing the substrate directly in a single bath containing $CuSO_4 . 5H_2O$ (1.44 10^{-2} molar) as the source of copper ions, disodiumtartrate (6.65 10^{-2} molar) as the complexing agent for Cu^{2+} ions, and NaOH to adjust the pH to the required value. For Al(1% Si) alloys the optimum pH is 10.5 at which the degradation of the substrate by the solution in the deposition bath is marginal. The useful pH range is limited from about 10.2 to about 11.0. Higher pH values result in more pronounced etching of the aluminum or aluminum alloy substrate and in a progressively worse adhesion of the copper layer to the substrate. At pH values below 10.2 the uniformity of the copper deposition deteriorates because of a progressively longer induction period before copper deposition starts.

The deposition bath is made up by mixing stock solutions of copper(II)sulphate and disodiumtartrate in deionized water, diluting this solution to about 3/4 of the final volume, adjusting the pH of this solution with NaOH, and finally by diluting this solution to the final volume with deionized water.

Using about the concentration ratio of $CuSO_4 . 5H_2O$/disodiumtartrate as mentioned hereabove in the example, excellent copper deposition on a substrate made of aluminum and/or aluminum alloys will be obtained for a broad concentration window of the copper (II) ions and tartrate in the solution. Doubling the concentrations of both Cu(II) and tartrate in the solution results in a marginally thicker copper layer on Al(1% Si) at a pH of 10.5. As described below, the thickness of the deposited copper layer is relatively insensitive to the immersion time. When the concentrations are five fold the original values, a further increase of thickness of the copper layer is observed but the pH of the solution has to be increased to 11.0 in order to get a uniform deposition of copper. This results however in copper layers with a worse adhesion to the aluminum alloy substrate. Lower concentrations of the Cu(II) ions and tartrate can also be used, but the throwing power of the deposition bath is reduced. As a consequence, the preferred concentration range of the copper(II) ions and tartrate extends preferably from about half the original concentration values to about two-fold these values. However, a copper deposition using the method of the present invention is also possible outside this specific range.

The mechanism of copper deposition on an Al containing substrate according to the present method is believed to be based on a substitution redox reaction occurring at the substrate surface. In this case, the second metal (Al) is oxidized at the surface and goes into the solution whereas the copper ions are reduced at the interface of the solution and the surface of the Al substrate and are deposited on the substrate. This deposition method does not need a previous treatment of the substrate in order to remove the native oxide layer. After copper deposition, only a minor concentration of oxygen is found at the interface between the copper layer and the Al substrate.

This is in contrast with autocatalytic copper deposition on aluminum using a formaldehyde-based deposition bath as known from the prior art. In the latter case, a thick oxide layer (Al_2O_3 and/or copper oxide) grows continuously between the deposited copper layer and the aluminum substrate during the deposition process.

Using the method of the present invention, a copper layer grows quickly on the aluminium substrate to a limited thickness. In a typical example of a 200 nm thick Al (1% Si) cold-sputtered alloy, a very fast deposition of 100 - 120 nm of copper occurs at room temperature with the above described deposition bath. In less than 2 minutes, the complete aluminum surface is covered with copper. After 2 minutes in the deposition bath, further copper deposition is almost negligible with a deposition rate of only 7 nm per minute (for up to 10 minutes deposition time).

In contrast with genuine electroless metal deposition baths, the process is not autocatalytic. As a consequence, after complete coverage of the aluminum substrate the copper growth comes to an end because of the lack of driving force which is the oxidation of the underlaying aluminum substrate. The advantage of the displacement plating process is that an exact control of the immersion time in the deposition bath is not necessary.

The present method of deposition on an Al substrate with copper is a selective deposition process being applicable at room temperature : when the substrate surface contains Al alloy structures together with non-conductive parts such as dielectric layers, only the Al parts will be covered with copper.

The present invention also relates to applications wherein said copper deposition method is used as a first step whereby a copper seed layer is deposited on an aluminum substrate for subsequent deposition of metals such as Ni or nickel alloys. This approach can be used for microelectronics applications.

Other possible applications include coverage of whole aluminum or aluminum alloy parts with copper for subsequent metal deposition in electroless or electrolytic baths.

Another application is the deposition of a protecting layer of copper in via holes in microelectronic circuits on top of aluminum for further selective autocatalytic electroless metal deposition with e.g. (copper or) nickel (alloys).

A further application of the method of the present invention is the electroless plating of metal bumps for flip-chip applications. In this case, a thick electroless Ni layer covered with a thin gold layer is plated on the immersion Cu layer/Al structure. The aluminum substrate layer is used for the bonding pad of integrated circuits.

Claims

1. Method for depositing copper or copper alloy on a second metal substrate made of aluminum or containing aluminum alloys comprising the steps of :

- preparing a solution containing a source of copper Cu(II) ions, a complexing agent for said Cu (II) ions and an additive to adjust the pH of the solution to a required value;
- immersing said metal substrate in said solution for a predetermined period whereby growing a copper layer on said second metal substrate.

2. Method according to claim 1, wherein the solution is an aqueous solution exempt of reductant.

3. Method according to claim 1 or 2, wherein the additive to adjust the pH is sodium hydroxide.

4. Method according to any one of the preceding claims, wherein the pH is adjusted to a value comprised between 10.0 and 11.5.

5. Method according to claim 4, wherein the pH is adjusted to a value comprised between 10.2 and 11.0, preferably around 10.5.

6. Method according to any one of the preceding claims, wherein the deposition of the copper or the copper alloy on an Al substrate is achieved by immersing said Al substrate in one single solution.

7. Method according to claim 6 further comprising the step of:

- removing the oxygen from said solution through bubbling an inert gas through said solution and
- immersing thereafter the aluminum substrate in the solution while keeping said solution under an inert gas atmosphere during the copper deposition.

8. Method according to claim 7, wherein the inert gas is Argon or Nitrogen.

9. Method according to any one of the preceding claims, wherein the Al alloy is Al(Si), Al(Cu), Al(Si, Cu) wherein the percentage of Si and/or Cu does not exceed 1% and 2% respectively.

10. Method according to any one of the preceding claims further comprising the step of:

- depositing a further metal layer such as nickel/gold or nickel after the deposition of the copper or copper alloy.

11. Method according to any one of the preceding claims characterized in that the deposition is performed at a temperature below 40°C and preferably at room temperature.

12. Method according to any one of the preceding claims characterized in that the ratio of the concentrations complexing agent/Cu(II) ions is higher than 2 and preferably around 4.6.

13. Method according to any one of the preceding claims characterized in that the concentration of Cu (II) ions in the solution is comprised in the range 0.7 10^{-2} to 7.2 10^{-2} molar.

14. Use of the method according to any one of the preceding claims for selective deposition of copper on a substrate having aluminum pattern and none non-conductive regions such as dielectric regions.

15. Use of the method according to any one of the preceding claims 1 to 13 for flip-chip applications.

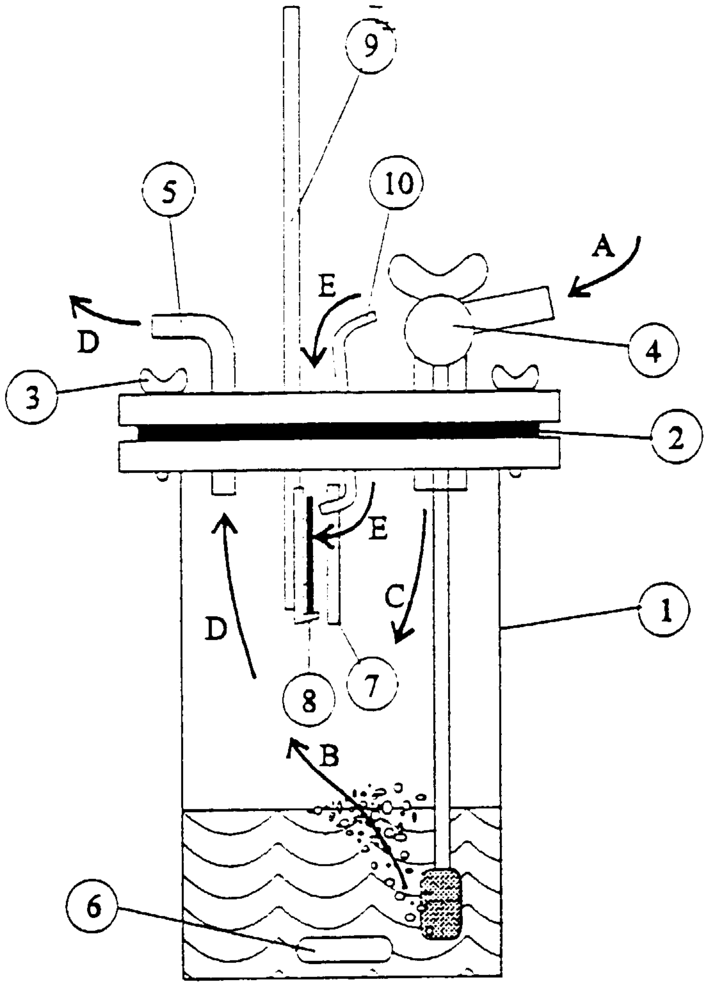

Fig. 1

European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 97 87 0063

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US 2 872 346 A (MILLER) 3 February 1959 * the whole document * ---	1-6, 10-13	C23C18/38
A	NL 7 900 504 A (MARIA JACOBA GERARDUS ANTONIUS) 25 July 1980 * page 2 * ---	7,8	
A	DATABASE INSPEC INSTITUTE OF ELECTRICAL ENGINEERS, STEVENAGE, GB Inspec No. 4967915, ASCHENBRENNER R ET AL: "Electroless nickel/copper plating as a new bump metallization" XP002038809 * abstract * & IEEE TRANSACTIONS ON COMPONENTS, PACKAGING AND MANUFACTURING TECHNOLOGY, PART B: ADVANCED PACKAGING, MAY 1995, USA, vol. 18, no. 2, ISSN 1070-9894, pages 334-338, -----	14,15	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C23C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	25 August 1997	Van Leeuwen, R

CATEGORY OF CITED DOCUMENTS

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