Abstract:

Title: METHOD OF PREVENTING OXIDATION AND METHOD OF PRODUCING A SEMICONDUCTOR PRODUCT

Fig. 1

A method for preventing oxidation of a copper or copper alloy surface to be used as an electronic material, the method having the steps of: providing a metal corrosion inhibitor comprising a nitrogen-containing heteroaromatic compound and an organic amine compound, the organic amine compound having a hydrocarbon portion and an amine portion, with the proviso that the organic amine compound is not an alkanolamine, and applying the metal corrosion inhibitor to the surface of copper or copper alloy.
DESCRIPTION

METHOD OF PREVENTING OXIDATION AND METHOD OF PRODUCING A SEMICONDUCTOR PRODUCT

TECHNICAL FIELD

The present invention relates to a method of preventing oxidation and a method of producing a semiconductor product.

BACKGROUND ART

With launching chip type components, a surface mount processing has occupied a major position for mounting components, in lieu of a conventionally employed processing of a through hall mount. In the surface mount system, a cream solder is printed on a substrate, and electronic components are placed thereon. The solder is then melted by giving infrared radiation or a hot air, thereby joining them. This processing tends however not to satisfy the recent requirements, even in a conventional packages like DIP (Dual Inline Package) and SOP (Small Outline Package), because the number of terminals has largely been increased for the sake of upgrade of the integration degree and diversification of the elements. Consequently, new packages have been introduced, such as QFG (Quad Flat Package) and LCC (Leaded Chip Carrier) having miniaturized terminals, and PGA (Pin Grid Array) which looks like a pin holder in which round pins are arranged in a reticular pattern on the bottom surface. Further, in a large-scale LSI, since thousands of connections to the outside are needed; the LSI employs a package with a high terminal density, e.g., BAG (Ball Grid Array).

Further, recently a flip chip mount of the bare chip is also proposed. In the process, the bare chip of a semiconductor can be mounted, as it is, i.e. without forming a package to seal a semiconductor chip in a resin. For example, using this technique, a
semiconductor light-emitting device or a semiconductor memory can be mounted via an efficient process, hiring neither a sealing process of the package, nor installation of a bonding wire therein.

For the above-described terminals of the chips and lead frames, to secure the electrical connection to the outside, copper or its alloy may frequently be used as an electrically conductive material. On the other hand, a surface of the copper material can easily be oxidized. Therefore, during the manufacturing process, it requires treatment for preventing oxidation degradation of the copper material surface, particularly in the case of temporary storage or transportation.

As a material for suppressing copper corrosion with preventing oxidation thereof, a solution containing an azole-series compound such as benzotriazole is proposed, to coat a copper surface by the compound (Non-Patent Literatures 1 and 2).

Further, in order to prevent oxidation degradation of the copper surface which is caused after CMP (Chemical Mechanical Polishing) processing, a chemical liquid containing an azole-series compound, an alkanolamine and the like is proposed (Patent Literatures 1 and 2).

CITATION LIST
Patent Literatures


Non-Patent Literatures

DISCLOSURE OF INVENTION

TECHNICAL PROBLEM

{0008}

As a protection material of the above-described terminal surface, a resin film can be considered to coat the surface for preventing oxidation degradation, on demand, in the processing stage. As this technique requires complicated processes such as coating and peeling of the film, a more efficient technique is desired. The techniques described in each of the above-described literatures, and the like are thus to be considered. In this regard, the present inventors experimentally confirmed the effect of the above techniques, but they have come to understand that simple application of the materials revealed in the literatures can not exert a sufficient oxidation-preventing property to the copper surface. On the other hand, in the electronic components for flip chip connection or the like in particular, the terminal in the component side is often constituted of a copper material, which may be easily oxidized, and a solder is placed thereon. Effective oxidation-preventing treatment is accordingly required, with respect to the terminal surface, precisely before the solder is applied thereto. Thus, the recent mounting process of the semiconductor element, as described above, particularly necessitates thorough enhancement of the oxidation-preventing performance.

The present invention addresses to the provision of a method for preventing oxidation capable of exerting an oxidation-preventing property to the surface of copper or copper alloy each of which is contained in an electronic material (hereinafter, these may be generically referred to as "a copper material"), and a method of producing a semiconductor product using the same.

SOLUTION TO PROBLEM

{0009}

The above problems can be solved by the following means.

{1} A method for preventing oxidation of a copper or copper alloy surface to be used as an electronic material, the method having the steps of:

providing a metal corrosion inhibitor having a nitrogen-containing heteroaromatic compound and an organic amine compound, the organic amine
compound having a hydrocarbon portion and an amine portion, with the proviso that the organic amine compound is not an alkanolamine; and

applying the metal corrosion inhibitor to the surface of copper or copper alloy.

{2} The method for preventing oxidation as described in the item {1},

wherein the hydrocarbon portion of the organic amine compound has an alkyl group having 1 to 10 carbon atoms.

{3} The method for preventing oxidation as described in the item {1} or {2},

wherein the content of the nitrogen-containing heteroaromatic compound in the metal corrosion inhibitor is from 0.01 to 5% by mass.

{4} The method for preventing oxidation as described in any one of the items {1} to {3},

wherein the content of the organic amine compound in the metal corrosion inhibitor is from 0.01 to 5% by mass.

{5} The method for preventing oxidation as described in any one of the items {1} to {4},

wherein the metal corrosion inhibitor further has a solvent that dissolves both the nitrogen-containing heteroaromatic compound and the organic amine compound, and wherein the solvent has an aqueous medium.

{6} The method for preventing oxidation as described in any one of the items {1} to {5},

wherein the organic amine compound has a Clog P value of 0 or higher.

{7} The method for preventing oxidation as described in any one of the items {1} to {6},

wherein the organic amine compound has benzyl amine, m-xylylenediamine, tert-butyl amine, n-hexyl amine, cyclohexyl amine, n-octyl amine, 2-ethylhexyl amine, 1-methylbutyl amine, or diethyl amine.

{8} The method for preventing oxidation as described in any one of the items {1} to {7},

wherein the nitrogen-containing heteroaromatic compound has an imidazole compound, a pyrazole compound, a triazole compound, a tetrazole compound, a pyridine compound or a quinoline compound.
The method for preventing oxidation as described in any one of the items \{1\} to \{8\},
wherein the content of the organic amine compound in the metal corrosion inhibitor is from 30 to 300 parts by mass with respect to 100 parts by mass of the nitrogen-containing heteroaromatic compound.

The method for preventing oxidation as described in any one of the items \{1\} to \{9\},
wherein the metal corrosion inhibitor further has a water-soluble organic solvent.

The method for preventing oxidation as described in any one of the items \{1\} to \{10\},
wherein the copper or copper alloy constitutes a terminal for placement of a solder.

The method for preventing oxidation as described in any one of the items \{1\} to \{11\},
wherein the metal corrosion inhibitor is applied to the copper or copper alloy surface by immersion, flow, drop or spray.

The method for preventing oxidation as described in any one of the items \{1\} to \{12\},
wherein the metal corrosion inhibitor is applied to the copper or copper alloy surface using single wafer cleaning equipment.

The method for preventing oxidation as described in any one of the items \{1\} to \{13\},
wherein the electronic material is a semiconductor element.

A method of producing a semiconductor product, the method having:
subjecting the copper or copper alloy surface of the semiconductor element to an oxidation-preventing treatment in accordance with the method of the item \{14\}, and producing a semiconductor product with the treated semiconductor element being mounted.

A semiconductor substrate product having:
a semiconductor substrate having a copper or copper alloy surface; and
a protective film formed on the surface, the protective film having a nitrogen-containing heteroaromatic compound and an organic amine compound, the organic amine compound having a hydrocarbon portion and an amine portion, with the proviso that the organic amine compound is not an alkanolamine.

5 {17} A metal corrosion inhibitor, for giving a property of preventing oxidation at a surface of copper or copper alloy, the metal corrosion inhibitor having: a nitrogen-containing heteroaromatic compound and an organic amine compound, the organic amine compound having a hydrocarbon portion and an amine portion, with the proviso that the organic amine compound is not an alkanolamine.

10 {18} The metal corrosion inhibitor as described in the item {17}, further having an aqueous medium for dissolving the nitrogen-containing heteroaromatic compound and the organic amine compound therein,

wherein the medium has an aqueous medium.

In the present specification, the term "having" is to be construed in the open-ended meaning as well as the term "comprising" or "containing." Further, the term "providing" broadly means, without any limitation in the inventive scope, to make the object ready to use, e.g., not only by synthesizing or producing the material, but also merely by purchasing it.

20 ADVANTAGEOUS EFFECTS OF INVENTION

{0010}

According to the present invention, it is possible to exert an oxidation-preventing property to the surface of a copper material which is contained in an electronic material. This largely enables enhancement of both manufacturing efficiency and manufacturing quality in the semiconductor production. Further, the method of the present invention is especially suitable for a flip chip mounting process of the bare chip which is proposed recently, and contributes to the improvement of both efficiency of the processing and product quality in the process.

Other and further features and advantages of the invention will appear more fully from the following description, appropriately referring to the accompanying drawing.
BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a main part-enlarged sectional view schematically showing one of preferable embodiments of the method according to the present invention.

Fig. 2 is a flow chart showing a procedure according to one of preferable embodiments of the method of the present invention.

MODE FOR CARRYING OUT THE INVENTION

Hereinafter, preferable embodiments of both the method and the metal corrosion inhibitor according to the present invention are explained in detail on the basis of Fig. 1 and Fig. 2 each of which is premised on a flip chip mounting of the bare chip. In the present embodiment, a body made of silicon is used as Semiconductor substrate 1, as shown in Fig. 1 (Process (a)). Layer of Ti or its alloy (Ti layer) 2 is formed thereon, and Layer of Cu or its alloy (Cu layer) 3 is formed through the Ti layer. The method of forming the Cu layer 3 is not particularly limited. One of examples of the method includes a film production by means of electroplating (Fig. 2 Process [I]).

As embodiments in which it is transported to the subsequent processing process without any change, an example thereof includes the embodiment in which solder layer (SnAg layer) 4 is formed on the surface of the Cu layer 3 in Process [V] through Process rout (1) in Fig. 2. It is preferred that the SnAg layer formed here is then melted moderately whereby a hemispherical solder bump is constituted. By proceeding to the next Process [VI] and conducting a reflow process, mounting or the like of a bare chip or an electronic component can be carried out through the solder bump.

A preferable embodiment according to the present invention takes Process rout (2) in Fig. 2. That is, in the present rout, member preservation in Process [IV] is carried out. There may be various causes for which such preservation (temporary storage) is carried out in this process. One example of the causes includes preservation for transportation in the time of moving it to another production facility or factory. Another
example includes temporary interruption of the production line due to a machine trouble. During these times, oxidation of the copper material becomes pronounced. In the present embodiment, for suppression or prevention of the oxidation, a particular metal corrosion inhibitor (a protective solution) is applied to the copper material surface of Semiconductor element 10 as Process [III]. According to the present embodiment, the surface of the copper material layer of the above-described Semiconductor element 10 is provided with a protective layer and the copper material is favorably prevented from contact with oxygen by this process, and as a result a good oxidation-preventing property can be exhibited. Subsequently, in order to rinse away an excessive metal corrosion inhibitor, a rinse is carried out (Process [III]). Hereinafter, the Process [II] and the metal corrosion inhibitor used therein are explained. Note that for the convenience of understanding, an embodiment in which Metal corrosion inhibitor S is shot out or sprayed from Nozzle S is shown in Fig. 1 as an example of the configuration in which the metal corrosion inhibitor is applied; however, the present invention is not construed as being limited to the embodiment.

{0015}

[Metal corrosion inhibitor (Protective solution)]

(Nitrogen-containing heteroaromatic compound)

The metal corrosion inhibitor of the present invention contains a nitrogen-containing heteroaromatic compound. As the nitrogen-containing heteroaromatic compound, those having a 5-membered ring structure or those having a 6-membered ring structure are preferred. As the nitrogen-containing heteroaromatic compound, an imidazole compound, a pyrazole compound, a triazole compound, a tetrazole compound, a pyridine compound, or a quinoline compound are more preferred. Herein, unless it is explicitly stated otherwise in the present specification, when it is called by putting the term "compound" at the end thereof, it means that derivatives which have been modified while maintaining the basic skeleton of the compound are incorporated therein. Typically, it means that structures in which any of the arbitrary substituents are put on the said compound are incorporated. The substituent is not particularly limited. Examples thereof include substituent T described below. Further, it means that in addition to the said compound, its salts and its ions, other than those above, are
incorporated.

The substituent T includes the following substituents.

The substituents include an alkyl group (preferably an alkyl group having 1 to 20 carbon atom(s), for example, methyl, ethyl, isopropyl, t-butyl, pentyl, heptyl, 1-ethylpentyl, benzyl, 2-ethoxyethyl, and 1-carboxymethyl), an alkenyl group (preferably an alkenyl group having 2 to 20 carbon atoms, for example, vinyl, allyl, and oleyl), an alkynyl group (preferably an alkynyl group having 2 to 20 carbon atoms, for example, ethynyl, butadiynyl, and phenylethynyl), a cycloalkyl group (preferably a cycloalkyl group having 3 to 20 carbon atoms, for example, cyclopropyl, cyclopentyl, cyclohexyl, and 4-methylcyclohexyl), an aryl group (preferably an aryl group having from 6 to 26 carbon atoms, for example, phenyl, 1-naphthyl, 4-methoxyphenyl, 2-chlorophenyl, and 3-methylphenyl), a heterocyclic group (preferably a heterocyclic group having 2 to 20 carbon atoms, more preferably a 5- or 6-membered heterocyclic group having at least one hetero atom selected from nitrogen, oxygen and sulfur atoms, for example, 2-pyridyl, 4-pyridyl, 2-imidazolyl, 2-benzimidazolyl, 2-thiazolyl, and 2-oxazolyl), an alkoxy group (preferably an alkoxy group having 1 to 20 carbon atom(s), for example, methoxy, ethoxy, isopropoxy, and benzylxy), an arylxy group (preferably an arylxy group having from 6 to 26 carbon atoms, for example, phenoxy, 1-naphthyloxy, 3-methylphenoxy, and 4-methoxyphenoxy), an alkoxycarbonyl group (preferably an alkoxycarbonyl group having 2 to 20 carbon atoms, for example, ethoxycarbonyl and 2-ethylhexyloxy carbonyl), an amino group (preferably an amino group, an alkylamino group or an aryl amino group having 0 to 20 carbon atom(s), for example, amino, N,N-dimethylamino, N,N-diethylamino, N-ethylamino, and anilino), a sulfamoyl group (preferably a sulfamoyl group having 0 to 20 carbon atom(s), for example, N,N-dimethylsulfamoyl, and N-phenylsulfamoyl), an acyl group (preferably an acyl group having 1 to 20 carbon atom(s), for example, acetyl, propionyl, butyryl and benzoyl), an acyloxy group (preferably an acyloxy group having 1 to 20 carbon atom(s), for example, acetoxy and benzoyloxy), a carbamoyl group (preferably a carbamoyl group having 1 to 20 carbon atom(s), for example, N,N-dimethylcarbamoyl and N-phenylcarbamoyl), an acylamino group (preferably an acylamino group having 1 to 20 carbon atom(s), for example, acetylamino and benzyolamino), a sulfonamide group
(preferably a sulfonamide group having 0 to 20 carbon atom(s) for example, methanesulfonamide, benzenesulfonamide, N-methylmethanesulfonamide, N-ethylbenzenesulfonamide), an alkylthio group (preferably an alkylthio group having 1 to 20 carbon atom(s), for example, methylthio, ethylthio, isopropylthio, benzylthio), an arylthio group (preferably an arylthio group having 6 to 26 carbon atoms, for example, phenylthio, 1-naphthylthio, 3-methylphenylthio, 4-methoxyphenylthio), an alkyl- or aryl-sulfonyl group (preferably an alkyl- or aryl-sulfonyl group having 1 to 20 carbon atoms, for example, methylsulfonyl, ethylsulfonyl, benzenesulfonyl), a hydroxyl group, a carboxyl group, a sulfo group, a cyano group, a halogen atom (for example, a chlorine atom, a bromine atom, and an iodine atom). Among them, an alkyl group, an alkenyl group, an aryl group, a heterocyclic group, an alkoxy group, an aryloxy group, an alkoxycarbonyl group, an amino group, an acylamino group, a hydroxyl group, and a halogen atom are more preferable. An alkyl group, an alkenyl group, a heterocyclic group, an alkoxy group, an alkoxycarbonyl group, an amino group, an acylamino group, and a hydroxyl group are particularly preferable.

Further, each of these groups exemplified as the substituent T may be substituted with the above-described substituent T.

In the present specification, the definitions of substitution groups should be construed in the broadest meaning. For example, when the terms "alkyl", "alkenyl", and "alkynyl" are used, unless otherwise particularly defined, those groups may be a straight chain, branched-chain, or cyclic.

As the nitrogen-containing heteroaromatic compound, a nitrogen-containing heteroaromatic compound which has 2 or greater nitrogen atoms in the molecule thereof and has a condensed ring structure is preferred, and a nitrogen-containing heteroaromatic compound which has 3 or greater nitrogen atoms in the molecule thereof and has a condensed ring structure is more preferred. Here, "2 or greater nitrogen atoms" or "3 or greater nitrogen atoms" are preferably atoms which constitute the condensed ring. As such nitrogen-containing heteroaromatic compound, an imidazole compound, a triazole compound, or a tetrazole compound is preferred.
As specific examples of the nitrogen-containing heteroaromatic compound, the
compound is more preferred that they are selected from imidazole, benzimidazole,
1,2,3-triazole, 1,2,4-triazole, benzotriazole, 1-[N,N-bis (hydroxyethyl) aminoethyl]
benzotriazole, 1-(1,2-dicarboxy ethyl) benzotriazole, tolyltriazole, tetrazole, 5-
aminotetrazole, and 1H-tetrazole-pentaacetic acid.

The nitrogen-containing heterocyclic aromatic compound is preferably
contained 0.0001% by mass or more, more preferably 0.001% by mass or more, and
particularly preferably 0.01% by mass or more, in the metal corrosion inhibitor. The
nitrogen-containing heterocyclic aromatic compound is preferably contained in the
upper limit of 25% by mass or less, more preferably 10% by mass or less, and
particularly preferably 5% by mass or less. By setting it to the above-described lower
limit or greater, effective oxidation-preventing property can be achieved. On the other
hand, by setting it to the above-described upper limit or less, storage stability can be
favorably exerted.

(Organic amine compound)

The metal corrosion inhibitor of the present invention contains an organic
amine compound except for an alkanolamine (amines having an alkyl group substituted
with a hydroxyl group), including, as a component, a hydrocarbon portion and an amine
portion. The above-described hydrocarbon portion refers to a portion (atomic group)
that is constituted of carbon and hydrogen. The portion may have Substituent Z. A
hydroxyl group or a hydroxyl group-containing group is not in the options of the
Substituent Z. As the Substituent Z, a carboxyl group, a sulfo group, alkoxy group, an
aryloxy, and a thiol group among the above-described substituent T are preferred.
Preferred ones among these groups have the same definitions as the substituent T. More
preferred examples of the hydrocarbon portion include an alkyl group (preferably
having 1 to 20 carbon atoms, more preferably having 1 to 10 carbon atoms), an aryl
group (preferably having 6 to 16 carbon atoms, more preferably having 6 to 10 carbon
atoms), and an alkenyl group (preferably having 2 to 30 carbon atoms, more preferably
having 2 to 10 carbon atoms). Each of the alkyl group, the aryl group and the alkenyl
group further may have the Substituent Z. Note that alkyl group is defined as including an aralkyl group. Note that the carbon number herein referred to is defined as the carbon number including the Substituent Z.

{0020}

The amine portion is a general term of including a primary amino group (-N¼), a secondary amino group (-NHR) and a tertiary amino group (-NR₂). Herein, R is an alkyl group (preferably 1 to 6 carbon atom(s)), an aryl group (preferably 6 to 24 carbon atoms), an alkenyl group (preferably 2 to 8 carbon atoms). Each of the alkyl group, the aryl group and the alkenyl group does not have a hydroxyl group or a hydroxyl group-containing group, but may have the Substituent Z. The carbon number means the number including the Substituent Z. Especially, a primary amino group and a secondary amino group are preferred and a primary amino group is particularly preferred.

{0021}

In the organic amine compound, although any number of the amine portion may be permitted, the number is preferably from 1 to 4, and more preferably 1 or 2.

{0022}

The organic amine compound preferably has a Clog P value of 0 or higher. Especially, it is preferred that the organic amine compound is an aliphatic organic amine compound having a Clog P value of 0 or higher. Further, the organic amine compound having a Clog P value of 0.5 or higher is more preferred. The upper limit of the ClogP value is not particularly limited, but normally 3 or less.

{0023}

In the present invention, the ClogP value is a value calculated using the computer program ChemDraw Ultra provided by CambridgeSoft Corporation. In the present invention, the value calculated using the ChemDraw Ultra (version:8.0 April 23, 2003) was used.

The term "ClogP value" as used herein means a common logarithmic value of partition coefficient P. The log P is a physical property value which represents as a quantitative numerical value how a certain organic compound is partitioned in the biphasic equilibrium system constituting of oil (generally 1-octanol) and water. The log
P is represented by the following equation.

\[ \log P = \log (C_{\text{oil}}/C_{\text{water}}) \]

In the equation, \( C_{\text{oil}} \) represents a molar concentration of a compound in the oil phase, and \( C_{\text{water}} \) represents a molar concentration of the compound in the aqueous phase.

The \( \log P \) means that across zero, if it positively increases, oil solubility increases, while if the absolute value of a minus figure increases, water solubility increases. The \( \log P \) is negatively correlated with water solubility of the organic compound and is widely used as a parameter to estimate for hydrophilicity and hydrophobicity of the organic compound.

In the present invention, it is preferred that the \( C_{\log P} \) value of the organic amine is 0 or higher, that is to say, the organic amine is relatively more hydrophobic. The reason for this, although it includes something that is not clear, is estimated as follows. It is expected that the nitrogen-containing heteroaromatic compound is adsorbed on the copper material surface to constitute an adsorbed film, to which the organic amine compound exerts the action. At this moment, the nitrogen-containing heteroaromatic compound is thought to form a correspondingly hydrophobic adsorbed film. It is supposed that this and the hydrocarbon portion of the organic amine compound exhibit a characteristic affinity, thereby forming a protective film with a relatively higher occlusive property. Also from this functional point of view, the organic amine compound having a hydroxyl group at the hydrocarbon portion thereof is considered to block the effects thereof. This action is thought to become more conspicuous when an aqueous medium is used as a medium.

Examples of the organic amine compound include, especially, ethyl amine, benzyl amine, diethyl amine, n-butyl amine, 3-methoxypropyl amine, tert-butyl amine, n-hexyl amine, cyclohexyl amine, n-octyl amine, 2-ethylhexyl amine, o-xylene diamine, m-xylene diamine, 1-methylbutyl amine, ethylene diamine (EDA), 1,3-propane diamine, 2-aminobenzyl amine, N-benzylethylene diamine, diethylene triamine, diethylenetriamine, N-methyl-N-butyl amine, p-xylylene diamine, N-(3-aminopropyl) morpholine, polyethylene imine, and polyallylamine.
The organic amine compound is preferably contained 0.001% by mass or more, more preferably 0.01% by mass or more, and particularly preferably 0.1% by mass or more, in the metal corrosion inhibitor. The organic amine compound is preferably contained in the upper limit of 50% by mass or less, more preferably 30% by mass or less, and particularly preferably 5% by mass or less. By setting it to the above-described lower limit or greater, better ability to prevent oxidation can be favorably exerted. On the other hand, by setting it to the above-described upper limit or less, an odor can be favorably reduced while effectively maintaining storage stability.

The organic amine compound, when it is defined in a relation with the above-described nitrogen-containing heteroaromatic compound, is preferably contained in an amount of equal to or greater than 10 parts by mass, more preferably equal to or greater than 20 parts by mass, and particularly preferably equal to or greater than 30 parts by mass, with respect to 100 parts by mass of the nitrogen-containing heteroaromatic compound, from the viewpoint of exerting ability to prevent oxidation. The organic amine compound is preferably contained in the upper limit of 1000 parts by mass or less, more preferably 500 parts by mass or less, and specifically preferably 300 parts by mass or less.

The reason why a good performance is achieved by a combination of the nitrogen-containing heteroaromatic compound and the organic amine compound in the present invention, as described above, includes unclarified aspects. However, this can be presumptively explained below in addition to those described above. That is to say, the nitrogen-containing heteroaromatic compound has a strong adsorptive property to the surface of the copper material. By formation of the adsorbed film (molecular film) thereof, contact between oxygen and the copper material is prevented, whereby antioxidant effects can be exhibited. However, the nitrogen-containing heteroaromatic compound is considered to be not completely densely-disposed on the surface of the copper material, whereby there exists an appreciable extent of gaps to which oxygen can penetrate. It is still presumed that according to the present invention, the above-
described organic amine compound is effectively entered into the gaps, or an adsorbed layer is formed in a manner such that the organic amine compound is laminated on a layer of the nitrogen-containing heteroaromatic compound, thereby blocking more efficiently penetration of oxygen. It is difficult to understand that such effect can be achieved by any of compounds, but it is understood that as the particular organic amine compound has a characteristic affinity to the nitrogen-containing heteroaromatic compound, a good synergistic effect between its oxidation prevention function and rinse-off property has been created, while maintaining a quality of the semiconductor product.

In the metal corrosion inhibitor of the present invention, aqueous medium is suitably used as its medium, and it is preferred that the metal corrosion inhibitor is an aqueous solution in which each component is uniformly dissolved. The content of water (aqueous medium) is preferably 50 to 99.5 mass%, and preferably 55 to 95 mass% relative to the total mass of the metal corrosion inhibitor. Thus, the case where water is a main component (50% by mass or more) is preferable from the viewpoints of inexpensive price and adjustment to environment, compared to the case of a high ratio of an organic solvent. Water (aqueous medium) may be an aqueous medium containing dissolved components, as long as they do not undermine the effectiveness of the present invention, or may contain inevitable trace mixed components. Especially, a clarified water such as distilled water, ion exchanged water, or ultrapure water is preferred, and ultrapure water that is used for semiconductor device production is particularly preferred.

Examples of the medium other than the above-described water include a mixed liquid with a water-soluble organic solvent (alcohol compound and the like) described below. In the present invention, it is preferred that the mixed liquid also contains water in the proportion of 50% by mass or more from a safety standpoint. Further, it is preferred that the water-soluble organic solvent has low surface tension and low viscosity, and uniformly disperses or dissolves in the aqueous medium. It is more
preferred that the water-soluble organic solvent uniformly dissolves in the
predetermined content thereof. Due to such low surface tension and low viscosity, the
water-soluble organic solvent acts as a chemical liquid which is more adapted for single
wafer type cleaning equipment.

The term "water-soluble organic solvent" refers to an organic solvent capable
of being mixed with water in an arbitrary proportion. Examples of the water-soluble
organic solvent include alcohol-compound solvents such as methyl alcohol, ethyl
alcohol, 1-propyl alcohol, 2-propyl alcohol, 2-butanol, ethylene glycol, propylene
glycol, glycerol, 1,6-hexanediol, cyclohexanediol, sorbitol, xylitol, 2-methyl-2,4-
pentanediol, 1,3-butandiol, and 1,4-butandiol, and ether-compound solvents such as
alkylene glycol alkyl ether (e.g. ethylene glycol monomethyl ether, diethylene glycol,
diethylene glycol, propylene glycol monomethyl ether, diethylene glycol monomethyl
ether, triethylene glycol, polyethylene glycol, propylene glycol monomethyl ether,
diethylene glycol monomethyl ether, tripropylene glycol monomethyl ether,
diethylene glycol monobuthyl ether, and diethylene glycol monobuthyl ether), amide
compound solvents, such as formamide, monomethylformamide, dimethylformamide,
acetamide, monomethylacetamide, dimethylacetamide, monoethyacetamide,
diethylacetamide, and N-methylpyrrolidone; sulfur-containing compound solvents, such
as dimethyl sulfone, dimethyl sulfoxide, and sulfolane; and lactone compound solvents,
such as γ-valerolactone and δ-valerolactone.

(Surfacetant)

The metal corrosion inhibitor of the present invention may further contain a
surfactant, may specifically contain an anionic surfactant and a nonionic surfactant.

• Anionic surfactant

The anionic surfactant, although it is not particularly limited, typically means a
compound having both a hydrophilic group and a lipophilic group in the molecule
thereof, in which a portion of the hydrophilic group dissociates in an aqueous solution
to become an anion or to take on the anionic character. Herein, the anionic surfactant
may exist as an acid with a hydrogen atom, or may be an anion resulting from
dissociation of the acid, or may be a salt of the acid. If it takes on the anionic character,
it may be a non-dissociative material, which also includes an acid ester and the like.

{0033}

In the above anionic surfactant, the anionic surfactant having 3 or more carbon
atoms is preferable, the anionic surfactant having 5 or more carbon atoms is more
preferable, and the anionic surfactant having 10 or more carbon atoms is specifically
preferable. Although there is no particular upper limit, the anionic surfactant having 40
or less carbon atoms is a practical limitation.

{0034}

Specific examples of the anionic surfactant having 10 to 40 carbon atoms
include a carboxylic compound having 10 to 40 carbon atoms, a phosphonate compound
having 10 to 40 carbon atoms, and a sulfonic acid compound having 10 to 40 carbon
atoms. Especially, an alkyl sulfonic acid, an alkylbenzene sulfonic acid, an
alkynaphthalene sulfonic acid, an alkyl diphenylether sulfonic acid (preferably
monosulfonic acid or disulfonic acid), an aliphatic acid amide sulfonic acid, a
polyoxyethylene alkylether carboxylic acid, a polyoxyethylene alkylether acetic acid, a
polyoxyethylene alkylether propionic acid, an alkyl phosphonic acid, an aliphatic acid,
and their salts are preferred. Among them, an alkyl diphenylether monosulfonic acid, an
alkyl diphenylether disulfonic acid, or their salts, or a mixture thereof are preferred.
Examples of the "salt" include an ammonium salt, a sodium salt, a potassium salt, and a
tetramethyl ammonium salt.

{0035}

• Nonionic surfactant

The nonionic surfactant has a hydrophobic group having 8 or more carbon
atoms and at least one hydrophilic group. The hydrophobic group is preferably selected
from an alkyl group having 14 or more carbon atoms, an alkynyl group, a cycloalkyl
group, an aryl group, a heterocyclic group, and a group in which two or more of these
groups are combined. As the hydrophilic group, those containing at least one of O, N,
or S atom are preferred. More preferable examples of the hydrophilic group include
those containing an ethylene oxide group or a propylene oxide group. A nonionic
surfactant is exemplified, which has a hydrophilic group with a total of at least 6 (preferably from 6 to 100) recurring units including the two groups as a component. In this case, the number of carbon atoms of the hydrophobic is preferably from 14 to 50, more preferably from 16 to 30. The total number of carbon atoms of ethylene oxide group or propylene oxide group is preferably an Integer of 12 to 1000, more preferably an Integer of 12 to 200.

Particular organic compound is preferably a compound which is represented by the following formulae.

Formula (A) \( R-(\text{CH}_2\text{CH}_20)_n\text{H} \)

Formula (B) \( R-(\text{CH}_2\text{CH}_2\text{CH}_20)_m\text{H} \)

Formula (C) \( R-(\text{CH}_2\text{CH}_20)_n(\text{CH}_2\text{CH}_2\text{CH}_20)_m\text{H} \)

\( R \) represents a linear or branched hydrocarbon group having a carbon number of 10 or more; \( n, m \) represents an Integer of 1 or more.

Examples of \( R \) include a straight chain, branched-chain, or cyclic, and substituted or unsubstituted alkyl group, an alkynyl group, a cycloalkyl group, an aryl group, a heterocyclic group, or a group that is made by combining at least two of these groups. Among them, a straight chain or branched-chain alkyl group is particularly preferred. Further, in the present specification, when it is called by putting the term "group" at the foot of the specific atomic group with respect to the substituent, the group means that the group may have further an arbitrary substituent.

\( n \) is preferably an Integer of 6 to 500, more preferably an Integer of 6 to 100.

\( m \) is preferably an Integer of 6 to 500, more preferably an Integer of 6 to 100.

The content of the surfactant in the metal corrosion inhibitor is not limited in particular, preferably contained in a range from 0.001 to 5% by mass, more preferably
from 0.01 to 3% by mass, and further preferably from 0.05 to 1% by mass with respect to the total mass of the metal corrosion inhibitor.

{0041}

[pH]

The pH of the metal corrosion inhibitor of present invention is not limited in particular, preferably pH 5 or more, more preferably pH 7 or more, and specifically preferably pH 9 or more. Although there is no particular upper limit, the pH 14 or less is a practical limitation.

{0042}

The above-described concentration of each component of the metal corrosion inhibitor is favorable at the time of treatment for protection, and the metal corrosion inhibitor may be concentrated for storage, distribution or the like. The concentration rate, although it may be determined as needed, is preferably from 1 to 50 times.

{0043}

[Kit]

The metal corrosion inhibitor of the present invention may be prepared in a form of a kit in which two or more raw materials are put in separate containers. Examples of the kit include an embodiment in which a liquid composition incorporating a nitrogen-containing heteroaromatic compound in an aqueous medium is prepared as a first liquid and a liquid composition incorporating an organic amine compound in an aqueous medium is prepared as a second liquid. As an example of its use, an embodiment is preferable in which the two liquids are mixed to prepare a metal corrosion inhibitor and then the metal corrosion inhibitor is applied on a timely basis to the above-described treatment for protection.

{0044}

(Material to be treated)

A target to which a treatment for oxidation prevention is subjected by using the above-described metal corrosion inhibitor is not particularly limited, and it is broadly applicable to electronic materials. In addition to a member surface of a copper material which is a component of the semiconductor element like the above-described embodiment, it is applicable to the following matters. That is, a treatment for protection
of a terminal (copper material) surface of a portion at which a solder bump is disposed in the package of the electronic components which are applied to BGA, or a terminal (copper material) surface at which a solder ball is disposed in CSP which is applied to a flip chip interconnection, is exemplified. In addition, this is preferably used for protection of copper material surface of the lead frame. In the present specification, the electronic material is used in a broad sense including a member in an electronic product, and it incorporates not only a semiconductor element (chip), but also a semiconductor substrate on the way to processing, a lead frame and the like.

Note that the method for preventing oxidation of the present invention is based on the premise that a metal corrosion inhibitor is applied to a copper material as described above. However, the metal corrosion inhibitor of the present invention is not prohibited from applying it to a transition metal other than copper (gold, platinum, nickel), a typical metal (aluminum), and the like.

(Processing type)

Although the processing equipment used in the present invention is not particularly limited, a single wafer type processing or batch processing equipment may be used. The single wafer type processing is a method of etching each wafer. One embodiment of the single wafer type processing is a method of processing by spreading a processing liquid entirely over the surface of a wafer using a spin coater. It is preferable that the liquid temperature of the metal corrosion inhibitor, the discharge rate of the metal corrosion inhibitor, and the rotation number of wafer of the spin coater are used by selecting appropriate values through selection of the wafer as a processing target.

In the present embodiment, although the processing condition is not componentarily limited, the processing by single wafer type processing equipment is preferred. In the processing by single wafer type processing equipment, semiconductor substrates are transported or rotated in the predetermined direction, and a metal corrosion inhibitor is discharged in a space between them to put the metal corrosion inhibitor on the semiconductor substrate. According to the necessity, metal corrosion
inhibitor may be sprayed while rotating the semiconductor substrate using a spin coater. On the other hand, in the batch-processing, a semiconductor substrate is immersed in a liquid bath constituted of a metal corrosion inhibitor to put the metal corrosion inhibitor on the semiconductor substrate. It is preferable for these processing types to be used appropriately and selectively depending on a structure, a material and the like of the device.

A temperature of metal corrosion inhibitor of treatment is described below is set to preferably from 15 to 40°C, and more preferably from 20 to 30°C. The supply rate of the metal corrosion inhibitor is not particularly limited, but is set to preferably from 0.3 to 3 L/min, and more preferably from 0.5 to 3 L/min. When the semiconductor substrate is rotated, it is preferable from the same view point as the above to rotate the semiconductor substrate at a rate from 100 to 1,000 rpm, even though the rate may depend on the size or the like of the semiconductor substrate.

(Rinse)

It is preferred that after application of the above-described metal corrosion inhibitor (protective liquid), an excess thereof is rinsed off with water or the like. The liquid to be used in rinse is preferably water. Examples thereof include an aqueous medium which has been explained in the section of the (Aqueous medium). The conditions for the rinse are not particularly limited. However, the rinse is preferably carried out at room temperature (about 25°C) in accordance with a method of discharging a liquid while supplying it directly from a liquid source (flow rate: from 0.5 to 3 L/min, for 10 to 60 seconds).

(Solder)

Formation of a solder layer that is carried out in the Process [V] in Fig. 2 may be performed in any manner, and it is possible to use an ordinary method that is applicable to this category of product. Regarding the kind of the solder, known solders may be used. For example, SnAg-based lead-free solder and SnAgCu-based solder may be used. The metal corrosion inhibitor according to the present invention is preferable
from the viewpoints that a good rinse-off performance due to rinse (Process [III]) is achieved and a solder-laying property is not excessively prohibited. The subsequent reflow (bonding) may be performed in accordance with ordinary conditions and procedures in this category of product (Process [VI]).

In the above, a processing for the copper material surface of the bare chip (semiconductor element) that is a particularly preferable embodiment of the present invention has been explained as an example thereof. However, the present invention is not construed as being limited by this. For example, in addition to the above, the present invention can be also favorably applied to protection of the terminal surface in the mounting of a package-type chip, and also to a processing for oxidation prevention of the copper material surface of the semiconductor substrate on the way to processing, the lead frame, and like.

In the present specification, the term "semiconductor substrate" is not only used to mean a silicon substrate (wafer), but also used in a broader meaning that includes a whole substrate structure on which a circuit structure is provided. The semiconductor substrate member or the member refers to a member that constitutes the above-defined semiconductor substrate, and may be composed of a single material or a plurality of materials. The processed semiconductor substrate may be called a semiconductor substrate product in order to distinguish it from a pre-processed semiconductor substrate. For further discrimination, if needed, a chip picked up by singulation after a processing of the semiconductor substrate product is called a semiconductor element or semiconductor device. That is, in a broad sense, the semiconductor element (semiconductor device) belongs to the semiconductor substrate product. Further, a product in which the semiconductor element is mounted is called a semiconductor product. The direction of the semiconductor substrate is not particularly limited. However, for convenience of description, in the present specification, the side of Cu layer 2 is specified as upside (upper side), while the side of substrate 1 is specified as lower side (bottom side). The structure of the semiconductor substrate or its members is illustrated in the attached figures by simplifying them. Accordingly,
they should be interpreted as an appropriate form, as needed.

EXAMPLES

{0052}

[Example 1 and Comparative Example 1]

The metal corrosion inhibitor (test liquids) designed to have components of each test No. and compositions (% by mass) shown in the following Table 1 were prepared.

{0053}

As a substrate, single crystal <100> silicon substrate (diameter: 12 inches, 300 mm) was used and a copper-plated film was provided thereon. A multilayer structure on the substrate was formed as follows. That is, in the order from the single crystal silicon side, a silicon oxide film (thickness: 100 nm), a copper film (thickness: 100 nm) produced by PVD, and a copper film (thickness: 3 µm) produced by electric plating were multilayered.

{0054}

<Test method>

(1) The chemical liquid which is the above-described metal corrosion inhibitor (test liquid) was dropped, using single wafer type cleaning equipment, onto the test substrate provided with the above-described copper film (25°C, rotation number: 500rpm, 2L/min., 20 seconds).

(2) After the processing, rinse with pure water (25°C, rotation number: 500rpm, 2L/min., 20 seconds) was carried out using the single wafer type cleaning equipment as well.

(3) Next, drying due to a high-speed rotation (1000rpm) was carried out using the single wafer type cleaning equipment.

(4) It was stored and left for 5 days under the conditions of room temperature and humidity of 60%RH in the atmosphere.

(5) Then, it was subjected to an annealing treatment at 150°C for 3 hours in the atmosphere.

(6) With respect to the copper-plated film provided on the test substrate after going through the processing of the above-described (1) to (5), measurement of copper oxide
film thickness was conducted in accordance with ellipsometry.

<Measurement method of pH>

Measurement of the test liquid immediately after preparation thereof (within about 2 minutes) was conducted at room temperature (25°C) using F-51 (trade name) manufactured by HORIBA, Ltd. As a result, the pH of each of samples was within the range of from 7 to 14.

{0055}
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<tr>
<th>Test No.</th>
<th>Species of compound</th>
<th>Concentration (mass%)</th>
<th>Component 1</th>
<th>Component 2</th>
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<td>CLogP: 0.89</td>
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DPG: Dipropylene glycol, PGMMME: Propylene glycol monomethyl ether
Table 1-continued

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<td>Component 4</td>
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</table>

DPG: Dipropylene glycol
PGMME: Propylene glycol monomethyl ether
As is apparent from the above-described results, the method for preventing oxidation and the metal corrosion inhibitor according to the present invention made it possible to exert a high oxidation prevention property to a copper material surface. It is seen that this largely enables enhancement of both manufacturing efficiency and manufacturing quality in the semiconductor production.

Further, a recycle test of each chemical liquid was conducted using the single wafer type cleaning equipment. As a result, it was confirmed that the same performance with respect to the each chemical liquid was obtained even by at least 3 times of the repeated use of the chemical liquid.

Having described our invention as related to the present embodiments, it is our intention that the invention not be limited by any of the details of the description, unless otherwise specified, but rather be construed broadly within its spirit and scope as set out in the accompanying claims.

This application claims priority on Patent Application No. 2012-181095 filed in Japan on August 17, 2012, which is entirely herein incorporated by reference.

REFERENCE SIGNS LIST

1 Semiconductor substrate
2 Ti layer
3 Cu layer
4 SnAg layer
5 Nozzle
10 Semiconductor element
S Metal corrosion inhibitor
CLAIMS

1. A method for preventing oxidation of a copper or copper alloy surface to be used as an electronic material, the method comprising the steps of:

   providing a metal corrosion inhibitor comprising a nitrogen-containing heteroaromatic compound and an organic amine compound, the organic amine compound having a hydrocarbon portion and an amine portion, with the proviso that the organic amine compound is not an alkanolamine; and

   applying the metal corrosion inhibitor to the surface of copper or copper alloy.

2. The method for preventing oxidation according to Claim 1, wherein the hydrocarbon portion of the organic amine compound comprises an alkyl group having 1 to 10 carbon atoms.

3. The method for preventing oxidation according to Claim 1 or 2, wherein the content of the nitrogen-containing heteroaromatic compound in the metal corrosion inhibitor is from 0.01 to 5% by mass.

4. The method for preventing oxidation according to any one of Claims 1 to 3, wherein the content of the organic amine compound in the metal corrosion inhibitor is from 0.01 to 5% by mass.

5. The method for preventing oxidation according to any one of Claims 1 to 4, wherein the metal corrosion inhibitor further comprises a solvent that dissolves both the nitrogen-containing heteroaromatic compound and the organic amine compound, and wherein the solvent comprises an aqueous medium.

6. The method for preventing oxidation according to any one of Claims 1 to 5, wherein the organic amine compound has a Clog P value of 0 or higher.

7. The method for preventing oxidation according to any one of Claims 1 to 6,
wherein the organic amine compound comprises benzyl amine, m-xylylenediamine, tert-butyl amine, n-hexyl amine, cyclohexyl amine, n-octyl amine, 2-ethylhexyl amine, 1-methylbutyl amine, or diethyl amine.

8. The method for preventing oxidation according to any one of Claims 1 to 7, wherein the nitrogen-containing heteroaromatic compound comprises an imidazole compound, a pyrazole compound, a triazole compound, a tetrazole compound, a pyridine compound or a quinoline compound.

9. The method for preventing oxidation according to any one of Claims 1 to 8, wherein the content of the organic amine compound in the metal corrosion inhibitor is from 30 to 300 parts by mass with respect to 100 parts by mass of the nitrogen-containing heteroaromatic compound.

10. The method for preventing oxidation according to any one of Claims 1 to 9, wherein the metal corrosion inhibitor further comprises a water-soluble organic solvent.

11. The method for preventing oxidation according to any one of Claims 1 to 10, wherein the copper or copper alloy constitutes a terminal for placement of a solder.

12. The method for preventing oxidation according to any one of Claims 1 to 11, wherein the metal corrosion inhibitor is applied to the copper or copper alloy surface by immersion, flow, drop or spray.

13. The method for preventing oxidation according to any one of Claims 1 to 12, wherein the metal corrosion inhibitor is applied to the copper or copper alloy
surface using single wafer type cleaning equipment.

14. The method for preventing oxidation according to any one of Claims 1 to 13, wherein the electronic material is a semiconductor element.

15. A method of producing a semiconductor product, the method comprising: subjecting the copper or copper alloy surface of the semiconductor element to an oxidation-preventing treatment in accordance with the method of Claim 14, and producing a semiconductor product with the treated semiconductor element being mounted.

16. A semiconductor substrate product comprising: a semiconductor substrate having a copper or copper alloy surface; and a protective film formed on the surface, the protective film comprising a nitrogen-containing heteroaromatic compound and an organic amine compound, the organic amine compound having a hydrocarbon portion and an amine portion, with the proviso that the organic amine compound is not an alkanolamine.

17. A metal corrosion inhibitor, for giving a property of preventing oxidation at a surface of copper or copper alloy, the metal corrosion inhibitor comprising: a nitrogen-containing heteroaromatic compound and an organic amine compound, the organic amine compound having a hydrocarbon portion and an amine portion, with the proviso that the organic amine compound is not an alkanolamine.

18. The metal corrosion inhibitor according to Claim 17, further comprising an aqueous medium for dissolving the nitrogen-containing heteroaromatic compound and the organic amine compound therein, wherein the medium comprises an aqueous medium.
AMENDED CLAIMS
received by the International Bureau on 25 December 2013 (25.12.13)

1. (amended) A method for preventing oxidation of a copper surface to be used as an electronic material, the method comprising the steps of:

   providing a metal corrosion inhibitor comprising a nitrogen-containing heteroaromatic compound and an organic amine compound, the organic amine compound having a hydrocarbon portion and an amine portion, with the proviso that the organic amine compound is not an alkanolamine; and

   applying the metal corrosion inhibitor to the surface of copper.

2. The method for preventing oxidation according to Claim 1, wherein the hydrocarbon portion of the organic amine compound comprises an alkyl group having 1 to 10 carbon atoms.

3. The method for preventing oxidation according to Claim 1 or 2, wherein the content of the nitrogen-containing heteroaromatic compound in the metal corrosion inhibitor is from 0.01 to 5% by mass.

4. The method for preventing oxidation according to any one of Claims 1 to 3, wherein the content of the organic amine compound in the metal corrosion inhibitor is from 0.01 to 5% by mass.

5. The method for preventing oxidation according to any one of Claims 1 to 4, wherein the metal corrosion inhibitor further comprises a solvent that dissolves both the nitrogen-containing heteroaromatic compound and the organic amine compound, and wherein the solvent comprises an aqueous medium.

6. (amended) The method for preventing oxidation according to any one of Claims 1 to 5, wherein the organic amine compound has a Clog P value of 0.5 or higher.

7. The method for preventing oxidation according to any one of Claims 1 to 6,
wherein the organic amine compound comprises benzyl amine, m-xylylenediamine, tert-butyl amine, n-hexyl amine, cyclohexyl amine, n-octyl amine, 2-ethylhexyl amine, 1-methylbutyl amine, or diethyl amine.

8. The method for preventing oxidation according to any one of Claims 1 to 7, wherein the nitrogen-containing heteroaromatic compound comprises an imidazole compound, a pyrazole compound, a triazole compound, a tetrazole compound, a pyridine compound or a quinoline compound.

9. The method for preventing oxidation according to any one of Claims 1 to 8, wherein the content of the organic amine compound in the metal corrosion inhibitor is from 30 to 300 parts by mass with respect to 100 parts by mass of the nitrogen-containing heteroaromatic compound.

10. The method for preventing oxidation according to any one of Claims 1 to 9, wherein the metal corrosion inhibitor further comprises a water-soluble organic solvent.

11. (amended) The method for preventing oxidation according to any one of Claims 1 to 10, wherein the copper constitutes a terminal for placement of a solder.

12. (amended) The method for preventing oxidation according to any one of Claims 1 to 11, wherein the metal corrosion inhibitor is applied to the copper surface by immersion, flow, drop or spray.

13. (amended) The method for preventing oxidation according to any one of Claims 1 to 12, wherein the metal corrosion inhibitor is applied to the copper surface using
single wafer type cleaning equipment.

14. The method for preventing oxidation according to any one of Claims 1 to 13, wherein the electronic material is a semiconductor element.

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15. (amended) A method of producing a semiconductor product, the method comprising:
subjecting the copper surface of the semiconductor element to a oxidation-preventing treatment in accordance with the method of Claim 14, and
producing a semiconductor product with the treated semiconductor element being mounted.

16. (amended) A semiconductor substrate product comprising:
a semiconductor substrate having a copper surface; and
a protective film formed on the surface, the protective film comprising a nitrogen-containing heteroaromatic compound and an organic amine compound, the organic amine compound having a hydrocarbon portion and an amine portion, with the proviso that the organic amine compound is not an alkanolamine.

17. (amended) A metal corrosion inhibitor, for giving a property of preventing oxidation at a surface of copper, the metal corrosion inhibitor comprising: a nitrogen-containing heteroaromatic compound and an organic amine compound, the organic amine compound having a hydrocarbon portion and an amine portion, with the proviso that the organic amine compound is not an alkanolamine;

wherein a phosphoric acid compound is not included in the metal corrosion inhibitor.

18. The metal corrosion inhibitor according to Claim 17, further comprising an aqueous medium for dissolving the nitrogen-containing heteroaromatic compound and the organic amine compound therein,

wherein the medium comprises an aqueous medium.
19. (added) The method for preventing oxidation according to any one of Claims 1 to 14, wherein the organic amine compound is 2-ethylhexyl amine.

20. (added) The method for preventing oxidation according to any one of Claims 1 to 14 and 19, wherein the organic amine compound is 2-ethylhexyl amine, and wherein the nitrogen-containing heteroaromatic compound is a triazole compound.

21. (added) The method for preventing oxidation according to any one of Claims 1 to 14, 19, and 20, wherein a phosphoric acid compound is not included in the corrosion inhibitor.

22. (added) The method for preventing oxidation according to any one of Claims 1 to 14 and 19 to 21, wherein oxidation of copper can be prevented within the range of a film thickness of copper oxide by 31 nm or less.

   (1) The chemical liquid which is the above-described metal corrosion inhibitor (test liquid) was dropped, using single wafer type cleaning equipment, onto the test substrate provided with the above-described copper film (25°C, rotation number: 500rpm, 2L/min., 20 seconds).

   (2) After the processing, rinse with pure water (25°C, rotation number: 500rpm, 2L/min., 20 seconds) was carried out using the single wafer type cleaning equipment as well.

   (3) Next, drying due to a high-speed rotation (1000rpm) was carried out using the single wafer type cleaning equipment.

   (4) It was stored and left for 5 days under the conditions of room temperature and humidity of 60%RH in the atmosphere.

   (5) Then, it was subjected to an annealing treatment at 150°C for 3 hours in the atmosphere.

   (6) With respect to the copper-plated film provided on the test substrate after going through the processing of the above-described (1) to (5), measurement of copper oxide film thickness was conducted in accordance with ellipsometry.
23. (added) The metal corrosion inhibitor according to Claim 17 or 18, wherein the organic amine compound is 2-ethylhexyl amine, and wherein the nitrogen-containing heteroaromatic compound is a triazole compound.
Fig. 1

Fig. 2

From previous process

(1) Film production of copper material by electric plating
   (EP-Cu)
   (2)

(II) Application of metal corrosion inhibitor (protective liquid)
(Treatment for copper material surface)

(III) Washing by water
(Rinse)

(IV) Preservation
(ex. 30°C, humidity of 60%RH, 3 days)

(V) Formation of solder layer (SnAg layer)

(VI) Reflow (bonding)
(ex. 150°C-1h, in atmosphere)

To next process
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

Int.Cl. C23 F11/00 (2006.01)i, H01 L2 1/60 (2006.01)i

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)

Int.Cl. C23 F11/00, H01 L2 1/60

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

- Published examined utility model applications of Japan 1952-1996
- Published unexamined utility model applications of Japan 1971-2013
- Registered utility model specifications of Japan 1996-2013
- Published registered utility model applications of Japan 1994-2013

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

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

<table>
<thead>
<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<tbody>
<tr>
<td>Y</td>
<td>JP 63-271961 A (Nippon Mining CO., LTD.) 1988.11.09, claims, page2 lower right column line3 - page3 upper left column line3 No Family</td>
<td>10, 11</td>
</tr>
<tr>
<td>Y</td>
<td>JP 8-274242 A (SANYO ELECTRIC CO., LTD.) 1996.10.18, claims1, 3,4,6, paragraphs [0009], [0017] No Family</td>
<td>11</td>
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