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[54] **METHOD OF ELECTROLESS METAL DEPOSITION**

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[58] **Field of Search** ..... 117/201, 212, 130 E, 227, 117/213

[56] **References Cited**

FOREIGN PATENTS OR APPLICATIONS

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[57] **ABSTRACT**

Method of electrolessly plating a body with a metal comprising placing the body in a work holder, depositing a film of a substance which catalyzes the deposition of the metal, on the surface to be plated, rinsing the body with a solution of a substance capable of chelating ions of the catalyst and then plating the surface electrolessly with the metal.

7 Claims, No Drawings

METHOD OF ELECTROLESS METAL DEPOSITION

BACKGROUND OF THE INVENTION

When a metal such as nickel is electrolessly deposited on a surface which is not normally a catalyst for such deposition, the surface must first be activated by treating it with a catalyst. Although a number of metals catalyze the electroless deposition of nickel, the one most often used is palladium. A very thin, discontinuous film of palladium particles is deposited, as a catalyzing medium, from a solution of a palladium salt.

In the manufacture of silicon semiconductor devices, for example, solderable electrodes are made by electrolessly depositing nickel on the electrode areas. It is customary to plate **40** or **50** silicon crystal slices simultaneously in a plastic basket. Some of the palladium salt solution becomes trapped in cracks and pores in the plastic basket and this causes subsequent deposition of nickel on the plastic surfaces. Since nickel is a catalyst for the electroless deposition of nickel, the unwanted nickel on the plastic basket can cause instability in the nickel plating bath.

One previous attempt to solve the problem of instability of the nickel plating bath was the addition of an ammonium salt to the nickel plating bath. Ammonium ions complex palladium ions and should therefore neutralize the effect of palladium ions dragged over into the nickel bath from the activation bath. When the palladium ions are complexed they can no longer be reduced to metallic palladium which acts as a catalyst for the deposition of nickel. However, this proved not to be a complete solution to the problem. Nickel still deposited on the plating basket and on the walls of the plating bath container.

The present invention resides in the discovery of the principle that if a substance which chelates the metal ion of the catalyst being used, is included in the rinse between the catalyst deposition and the metal plating, unwanted metal plating on the plating basket (or other work holder) and on the walls of the bath container, is almost eliminated.

DESCRIPTION OF PREFERRED EMBODIMENT

An example of the improved process of the present invention, applied to the nickel plating of silicon semiconductor devices, is as follows.

The objects being plated are crystal slices of semiconducting silicon in which a multiplicity of devices such as transistors are being fabricated. Monolithic type integrated circuits can also be made in this way. Each slice has a layer of silicon dioxide covering one surface except where ohmic contacts are to be made to electrode areas. Openings through the silicon dioxide over the electrode areas are assumed to have previously been made using conventional photoresist, exposure and developing techniques followed by etching away the unwanted areas of silicon dioxide. The remaining hardened photoresist has then been removed.

In preparing the slices to be nickel plated on the electrode contact areas, the silicon slices are etched lightly with a solution such as the following:

Glacial acetic acid	950 ml/liter
48% HF	50 ml/liter

The slices are immersed in the solution for only 20 seconds at room temperature (25° C). This etch does not remove much of the silicon dioxide protective coating, since the coating has been made thick enough to withstand light etching treatments. In treating the slices in this and subsequent steps, about 40 or 50 slices at a time are held in a basket made of a plastic such as polypropylene. Inert work holders made of other plastics or of other materials such as glass, can also be used. The surfaces of the work holder must be of a material that does not catalyze the electroless deposition of the metal being deposited.

The slices are then treated with a solution of a salt of a metal which is a catalyst for the deposition of nickel. An example of such a solution is:

Glacial acetic acid	948 ml/liter
48% HF	50 ml/liter
5% by wt. $PdCl_2$	2 ml/liter

The amount of $PdCl_2$ solution may be varied between about 0.5 and 10 ml/liter. If too much $PdCl_2$ is present, the deposit of palladium metal tends to become non-uniform and this leads to non-uniformity in the nickel deposit.

The amount of 48% HF can be varied between about 20 and 150 ml/liter. The glacial acetic acid and the hydrofluoric acid improve the wetting of the silicon surface by the palladium solution and thus permit more uniform deposition of palladium at low concentration. This saves palladium.

The slices are immersed in the above catalyst solution for 20 seconds at 25° C. The time can be varied between about 5 seconds and 60 seconds. The solution is reduced by the silicon, and palladium deposits mostly on the silicon and not on the silicon dioxide. However, some palladium does occasionally deposit on the oxide. Palladium also does not normally deposit on the plastic basket but some palladium solution usually becomes trapped in pores and cracks of the basket and this palladium cannot later be removed by rinsing.

Next, the slices are rinsed with a solution which contains an ammonium salt and, preferably, a silicon wetting agent. An example of this solution is:

2 propanol	200 ml
ammonium acetate	20 g
deionized water	800 ml

The slices are immersed in this solution for 25 seconds at 25° C. Immersion time may be between about 10 and 45 seconds. The propanol is used as a wetting agent. Other wetting agents, such as other low molecular weight alcohols (i.e., up to C_7), may be substituted. Actually, higher molecular weight alcohols than C_7 alcohols can be used, less preferably, and as the molecular weight increases, the amount used decreases. The ammonium acetate may be used in any amount greater than about 20 g/liter up to saturation. Other ammonium salts such as ammonium citrate may also be used. Chelating agents other than ammonium salts may also be used. The main criterion is that the amount of chelating agent necessary to complex the palladium must not be so great that the nickel plating rate is slowed down unduly.

This solution complexes any palladium salt that may have been trapped in the plating basket or on the slice

and thus prevents that palladium from being reduced to palladium metal which would catalyze the deposition of nickel on surfaces where it is not wanted. The ammonium ion does not complex the palladium metal deposited on the silicon slices.

After treatment with the rinse solution, the slices are immersed in a nickel plating bath which may have a composition such as the following, per liter of solution. The solvent used is deionized water.

Potassium glycolate	78 g
Nickel sulfate	36 g
Ammonium acetate	10 g
Sodium hypophosphite	15 g
Sulfuric acid	to pH 4.8 – 4.9

The slices are immersed in this solution for 3 minutes at 80° C. The glycolate and the acetate are chelating agents. Other chelating agents may be used. The ammonium acetate is included to complex any palladium salt that may have been dragged over from the palladium catalyst solution despite thorough rinsing. The glycolate complexes the nickel. Any soluble nickel salt may be used and the concentration is not critical. Any conventional reducing agent for nickel may be used in place of the hypophosphite. Other examples are amine boranes and hydrozine. The pH range may be either 3.8 – 5.1 or 7.5 – 10.5 and the pH may be adjusted with other acids or alkalies.

If the surface being plated is not one which is capable of reducing the catalyst ion, a coating of a sensitizing agent, such as tin, must first be deposited. This must be done, for example, when the substrate being plated is glass or a plastic. In this case, since the work holder also will be sensitized and this would lead eventually to it being completely coated with metal, the work holder should be changed between the sensitization step and the activation step.

The method applies to any metal capable of being electrolessly deposited. Cobalt and copper are examples of metals other than nickel.

The method also applies to any of the catalysts which are conventional for depositing these metals. Platinum, rhodium and iridium are other examples.

I claim:

1. A method of electrolessly depositing a metal on a surface of a body comprising:

supporting said body on an inert work holder made of a material which does not catalyze the electroless deposition of said metal,

treating said surface and said work holder with a solution containing a substance which catalyzes the electroless deposition of said metal,

rinsing said surface and said work holder with a solution of a substance that chelates ions of the catalyst, and

treating said surface with a plating bath comprising a salt of said metal, a reducing agent for said metal salt, a complexing agent for ions of said metal, and a pH adjusting agent.

2. A method according to claim **1** in which said catalyst is palladium and the substance which chelates palladium ions is an ammonium salt.

3. A method according to claim **2** in which said body is silicon and in which the silicon body has a coating of silicon dioxide except where metal is to be deposited.

4. A method according to claim **3** in which said metal is nickel and the surface to be nickel plated is first lightly etched prior to treatment with the palladium solution.

5. A method according to claim **1** in which said rinsing solution also contains a wetting agent.

6. A method according to claim **5** in which the wetting agent is a low molecular weight alcohol.

7. A method according to claim **1** in which the surface being coated is silicon and said catalyzing solution also contains hydrofluoric acid and acetic acid.

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