BORIC ACID REPLENISHMENT IN ELECTROPLATING BATHS

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Related U.S. Application Data

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ABSTRACT

Boric acid is replenished in an electroplating bath via a replenishment solution comprising boric acid dissolved in pure water, in which the solubility at room temperature is comparable to that in the plating bath at operating temperature. The replenishment solution may be used to replace all or part of the water lost by evaporation. An automated device may be used to replenish boric acid in the electroplating bath.
BORIC ACID REPLENISHMENT IN ELECTROPLATING BATHS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Application No. 61/395,290 filed May 10, 2010, which has the same inventors.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] This invention is concerned with control of electroplating processes, and in particular with replenishing buffering agents in electroplating baths.

[0004] 2. Description of the Related Art

[0005] Nickel electroplating baths are widely used in industry to fabricate a wide variety of products ranging from microelectronic integrated circuit (IC) chips to rocket engines. Sulfamate baths typically comprise 300-450 g/L nickel sulfate [Ni(SO₄)₂·6H₂O], 0-30 g/L nickel chloride [NiCl₂·6H₂O] and 30-45 g/L boric acid [H₃BO₃], and are operated at a pH in the 3.5-5.0 range and a temperature in the 30-60°C range. Watts nickel baths typically comprise 225-400 g/L nickel sulfate [NiSO₄·6H₂O], 30-60 g/L nickel chloride and 30-45 g/L boric acid, and are operated at a pH in the 2-4.5 range and a temperature in the 45-65°C range. Either type of nickel bath may comprise nickel bromide instead of nickel chloride. Boric acid functions as a buffering agent to prevent pH excursions at the cathode surface that can degrade the quality of the electrodeposit. Note that the hydrogen evolution side reaction during the nickel electrodeposition process consumes protons and tends to raise the pH of the solution near the cathode, which can result in formation of nickel hydroxide particulates. Both types of nickel electroplating baths may also contain wetting agents and/or organic additives.

[0006] Replenishment of boric acid lost from the bath via drogout with the plated parts, chemical/electrochemical decomposition and precipitation associated with water evaporation presents a problem since the solubility of boric acid in the bath at room temperature is about 30 g/L whereas the preferred boric acid concentration is typically 30-45 g/L. The lower solubility in the bath at room temperature generally precludes use of bath concentrates for boric acid replenishment. Furthermore, boric acid dissolves very slowly in the plating bath even at elevated temperatures so that replenishment by addition of solid boric acid to the bath tends to disrupt production and may introduce very small boric acid particles that can degrade the deposit properties.

[0007] One currently-used approach to addressing the problem of boric acid replenishment is to hang one or more cloth bags containing boric acid in the bath so that boric acid is continuously leached into the bath. A difficulty in this case is that the relatively coarse cloth mesh size needed to provide a sufficient leach rate may allow finer boric acid particles generated during boric acid dissolution to enter the bath. This approach also does not provide adequate control of the replenishment rate.

SUMMARY OF THE INVENTION

[0008] The invention provides a method and an apparatus for replenishing boric acid in an electroplating bath, a sulfamate nickel or a Watts nickel bath, for example. In the method of the invention, boric acid is dissolved in substantially pure water to provide a replenishment solution that is added to the electroplating bath to compensate for boric acid losses due to drogout, precipitation resulting from water evaporation, and chemical and electrochemical decomposition, for example. Since the solubility of boric acid in pure water at room temperature is more than 45 g/L, the boric acid concentration in the electroplating bath can readily be maintained at even 45 g/L via addition of the replenishment solution to compensate for water lost by evaporation.

DETAILED DESCRIPTION OF THE INVENTION

[0009] Technical terms used in this document are generally known to those skilled in the art. The terms “electroplating” and “plating” are equivalent.

[0010] The invention provides a method and an apparatus for replenishing boric acid in an electroplating bath. The invention is particularly useful for control of plating baths that operate at an elevated temperature, sulfamate nickel baths, for example, which are typically operated in the temperature range from 30 to 60°C.

[0011] In one embodiment, the method of the invention for replenishing boric acid in an electroplating bath, comprises the steps of: providing a replenishment solution comprising a predetermined concentration of boric acid dissolved in substantially pure water; and adding a predetermined volume of the replenishment solution to the plating bath so as to maintain the concentration of boric acid in the plating bath substantially at a target boric acid concentration. In the simplest case, the replenishment solution is used to compensate for both drogout of the plating bath and water lost by evaporation so that the predetermined volume of the replenishment solution added to the plating bath is equivalent to the decrease in the volume of the plating bath volume during a given time interval. In this case, sufficient replenishment solution is added periodically, continuously or intermittently to maintain the plating bath level substantially constant, based on an index mark or a bath level indicator, for example. The predetermined volume of the replenishment solution to be added to the plating bath may also be determined based on analysis of the boric acid concentration in the plating bath, measurement of the liquid level in the plating bath tank, or preferably both. Alternatively, the predetermined volume of the replenishment solution to be added to the plating bath may be estimated based on product throughput (amp-hours of charge) during a given time interval, water evaporation rate for the particular plating bath tank, or preferably both. The boric acid replenishment solution may be used to compensate for all or part of the water lost from the plating bath by evaporation.

[0012] The predetermined concentration of boric acid in the replenishment solution may be any concentration consistent with the replenishment scheme used but will typically be in the 30-45 g/L range. It may be advantageous for the concentration of boric acid in the replenishment solution to be equal to or greater than the target boric acid concentration in the plating bath.

[0013] In another embodiment, the method of the invention for replenishing boric acid in an electroplating bath, comprises the steps of: providing a replenishment solution comprising a predetermined concentration of boric acid dissolved in substantially pure water; and flowing the replenishment solution from a replenishment solution reservoir into the plating bath at a predetermined flow rate so as to maintain the concentration of boric acid in the plating bath substantially at...
a target boric acid concentration. In the simplest case, the replenishment solution is used to compensate for both dra... read-only memory (PROM) chip, a magnetic storage device, a computer disk (CD), a digital video disk (DVD), and combinations thereof. The memory element may be separate or be included in the computing device.

DESCRIPTION OF A PREFERRED EMBODIMENT

[0018] A typical sulfamate nickel bath for plating semiconductor wafers comprises 30-45 g/L boric acid and operates at 50°C, and loses more water to evaporation (up to 15 liters/day) than to dragout (typically 0.5-1.0 L for 100 wafers/day). By using a replenishment solution comprising 45 g/L boric acid to replace all or a portion of the water lost to evaporation, all boric acid losses, including those due to precipitation and decomposition, can readily be compensated so as to maintain the boric acid concentration in the bath at a target value. Boric acid is preferably replenished using a combination of relatively concentrated replenishment solution and substantially pure water, or a less concentrated replenishment solution.

[0019] As an example, consider a nickel plating bath that is operated at 50°C and 45 g/L boric acid and is used to plate 100 semiconductor wafers per day. Each wafer typically drags in a volume of rinse water equal to the volume of plating bath that it drags out so that the effect of dragout on the total volume of the plating bath is negligible. For a typical dragout rate of 10 mL per wafer and a throughput of 100 wafers per day (dragout volume of 1000 mL per day), 45 g of boric acid are lost per day to dragout and must be replenished without increasing the total volume of the plating bath. This can be accomplished according to the invention by adding 1000 mL per day of a replenishment solution comprising 45 g/L boric acid to partially compensate for 1000 mL of the water lost to evaporation, which is typically 3000 mL per day. The remaining 2000 mL per day of evaporated water may be replenished by addition de-ionized water and/or concentrates for replenishment of other plating bath constituents depleted by dragout.

We claim:

1. A method of replenishing boric acid in a plating bath, comprising the steps of:
   providing a replenishment solution comprising a predetermined concentration of boric acid dissolved in substantially pure water; and
   adding a predetermined volume of the replenishment solution to the plating bath so as to maintain the concentration of boric acid in the plating bath substantially at a target boric acid concentration.

2. The method of claim 1, wherein the plating bath is a nickel plating bath operated in the temperature range from 30 to 65°C.

3. The method of claim 1, wherein the predetermined concentration of boric acid in the replenishment solution is in the 30-45 g/L range.

4. The method of claim 1, wherein the predetermined concentration of boric acid in the replenishment solution is equal to or greater than the target boric acid concentration in the plating bath.

5. A method of replenishing boric acid in a plating bath, comprising the steps of:
   providing a replenishment solution comprising a predetermined concentration of boric acid dissolved in substantially pure water; and
   flowing the replenishment solution from a replenishment solution reservoir into the plating bath at a predeter-
mended flow rate so as to maintain the concentration of boric acid in the plating bath substantially at a target boric acid concentration.

6. The method of claim 5, wherein the plating bath is a nickel plating bath operated in the temperature range from 30 to 65°C.

7. The method of claim 5, wherein the predetermined concentration of boric acid in the replenishment solution is in the 30-45 g/L range.

8. The method of claim 5, wherein the predetermined concentration of boric acid in the replenishment solution is equal to or greater than the target boric acid concentration in the plating bath.

9. An apparatus for replenishing boric acid in a plating bath, comprising:
   a reservoir containing a replenishment solution comprising a predetermined concentration of boric acid dissolved in substantially pure water;
   a means of transferring a predetermined volume of the replenishment solution from the reservoir to the plating bath; and
   a computing device having a memory element with a stored algorithm operative to effect, via appropriate interfacing, transfer of the predetermined volume of the replenishment solution from the reservoir to the plating bath so as to maintain the concentration of boric acid in the plating bath substantially at a target boric acid concentration.

10. The apparatus of claim 9, wherein the computing device is further operative to determine the predetermined volume of the replenishment solution to be added to the plating bath based on an analysis of the boric acid concentration in the plating bath.

11. The apparatus of claim 9, wherein the computing device is further operative to determine the predetermined volume of the replenishment solution to be added to the plating bath based on a volume of water lost from the plating bath by evaporation.

12. The apparatus of claim 9, further comprising:
   a bath level indicator.

13. The apparatus of claim 9, further comprising:
   a means of adding a predetermined volume of substantially pure water to the plating bath.

14. The apparatus of claim 13, wherein the computing device is further operative to determine the predetermined volume of substantially pure water to be added to the plating bath based on the predetermined volume of the replenishment solution and a volume of water lost from the plating bath by evaporation.

15. The apparatus of claim 9, wherein the memory element is selected from the group consisting of computer hard drive, microprocessor chip, read-only memory (ROM) chip, programmable read-only memory (PROM) chip, magnetic storage device, computer disk (CD), digital video disk (DVD), and combinations thereof.