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ELECTROPLATING WITH ANTIMONY

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1 Claim. (Cl. 204—45)

This invention relates to the electrodeposition of antimony and in one specific embodiment to such electrodeposition on germanium.

It is well known that antimony may be electrically deposited from antimony fluoride solutions. See F. C. Mathers, Transactions of Electrochemical Society, 31, pages 289–293. Attempts to deposit antimony out of such solutions on certain materials such as, for example germanium, however, result in a non-uniform deposit, some crystal faces being plated and others not. The selective plating effect out of acidic solutions has been minimized by the use of weaker organic acid baths such as complex citrate baths. See "Antimony Plating" by K. Gustaf Soderberg and H. L. Pinkerton, "Plating" magazine, March 1950 at page 254 et seq. However, the use of this complex organic bath does not result in a uniform antimony coating on germanium, due to the very poor cleaning action, that is, the relative inability of such baths to dissolve the oxide usually present on the germanium surface.

It has been found that plating out of an alkaline solution of antimony salts according to the method of the present invention produces a smooth, uniform, adherent layer far superior to that produced by any of the previously proposed methods. This method involves preliminary cleaning of the body to be plated, first by degreasing in any commercial anodic or cathodic cleaner, such as a boiling 10 per cent caustic solution, rinsing in water, immersion in hydrofluoric acid to get rid of surface contaminants and electroplating in an alkaline solution of antimony.

The following specific examples will illustrate procedures by which the present invention may be practiced.

Example 1

A slab of germanium containing no more than 1 per cent impurities and having a surface area of about 1 square inch, was degreased by immersion in a boiling solution of 10 per cent caustic soda for from 15 to 30 seconds, was then rinsed in water and immersed in a 1:1 solution of 40 per cent hydrofluoric acid and water for 15 to 30 seconds at room temperature. After rinsing, the germanium slab was plated in a solution prepared by adding a quarter pound of antimony trichloride to 4 liters of distilled water, boiling to convert it to antimony trioxide, which precipitate after being washed with distilled water several times by decantation, was dissolved in a solution of two pounds of potassium hydroxide in 3 liters of water and boiled for 5 hours. To the resulting solution then was added between 0.15 and 0.30 gram per liter of bone glue. The plating procedure was carried out at a temperature of between 190° F. and 200° F. with the germanium body acting as the cathode. Since it was desired to plate both sides of the germanium body, two antimony anodes, one on either side of the body to be plated, were used. A voltage of about 3 volts was impressed between the cathode and each of the anodes to produce a current density of about 350 milliamperes per square inch for about 1 minute, 15 seconds. The plated body was first rinsed in tap water, then with distilled water and then with denatured ethyl alcohol containing methyl alcohol as a denaturant to facilitate drying. The resultant plating was about 1/10 of a mil thick.

The solution used in Example 1 was of a concentration of about 18 grams of antimony per liter of aqueous potassium hydroxide solution. It has been found that concentrations lower than 15 grams per liter seriously decrease the plating rate and impair the efficiency. Although it is preferable to use higher antimony concentrations, it is difficult to produce concentrations very much higher than 18 grams per liter in a bath made from antimony salts. It has been found that the antimony content of the bath may be increased electrolytically using a porous pot filled with potassium hydroxide solution around the cathode to prevent deposition. A procedure by which such a concentrated bath was produced is described in Example 2.

Example 2

The procedure described in Example 1 was carried out except that instead of preparing the bath by dissolving antimony trioxide in a potassium hydroxide solution, it was produced in the following manner: A 1-liter bath was made with an aqueous solution of 300 grams of potassium hydroxide per liter using two antimony anodes and surrounding the cathode with a porous pot. A potential of about 3 volts was maintained across the electrodes for a period of 14 hours. A solution of 22.6 grams of antimony per liter of potassium hydroxide resulted. This solution produced smooth, firmly adherent, continuous coatings of antimony similar to those produced by the process of Example 1.

Although the best results have been obtained at the plating temperature range of from about 190° F. to 200° F. and with current densities of from 350 to 700 milliamperes per square inch, the process operates satisfactorily at temperatures as low as 100° F. The use of temperatures lower than 100° F. results in poor efficiency and selective plating. Temperatures of above 200° F. are just as useful as the range described in the examples although loss of solution through evaporation becomes a factor as the boiling point of about 220° F. is approached. The upper temperature limit coincides with the boiling point of the solution. Satisfactory current densities which should be maintained during the procedure vary somewhat with the temperature of the solution ranging from a minimum of about 35 milliamperes per square inch at 120° F. to a maximum of about 1000 milliamperes per square inch at temperatures close to boiling. This range is for a bath prepared in accordance with Example 1. As the concentration of the bath is increased the upper current density limit increases somewhat so that with a concentration of about 25 grams per liter of potassium hydroxide at a temperature near boiling a current density as high as 1500 milliamperes per square inch may be used.

Other variables of the procedures described will be immediately perceivable to those skilled in the art. For example, where it is not desired to plate the body on more than one side, one antimony anode will be sufficient. Where the surface area to be plated is large, anodes may be shaped accordingly or several anodes may be placed so as to produce a uniform coating over the entire surface. As is well known in the art a "thief" may be used to maintain uniform coating thickness over an entire base so as to prevent an accumulation of material at the edges. The use of bone glue to improve the appearance of the deposit is well known and any other collodial addition agent intended for this purpose may be substituted.

The process described is not limited to the production of deposits one-tenth of a mil thick or thinner, coatings of 1 mil in thickness and more being readily obtainable by extending the plating time and without otherwise modify-

ing the procedure described. Although deposits more than 1 mil in thickness may also be produced, it is preferable to use a thief to prevent an accumulation of material at the edges where such coatings are desired.

Although the invention has been described in terms of its specific embodiments, certain modifications and equivalents will be apparent to those skilled in the art and are intended to be included within the scope of the invention.

What is claimed is:

The method of electroplating a body of germanium with antimony which comprises immersing the said body and at least one antimony electrode in a solution of antimony in aqueous potassium hydroxide, said solution containing from 15 to 25 grams of antimony per liter of potassium hydroxide solution while maintaining the temperature of the aforesaid solution at between 190° F. and

200° F., impressing a potential between the said germanium body and said at least one antimony electrode so that the germanium body is at a negative potential in respect to the said at least one antimony electrode to maintain a current density of between 350 and 700 milliamperes per square inch of surface area of the germanium body.

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