

[54] **METHOD OF DETERMINING  
CONCENTRATIONS**

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**204/1 T, 195 R, 195 G, 195 F**

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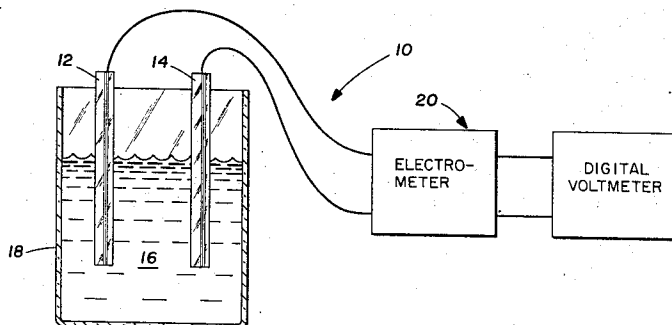
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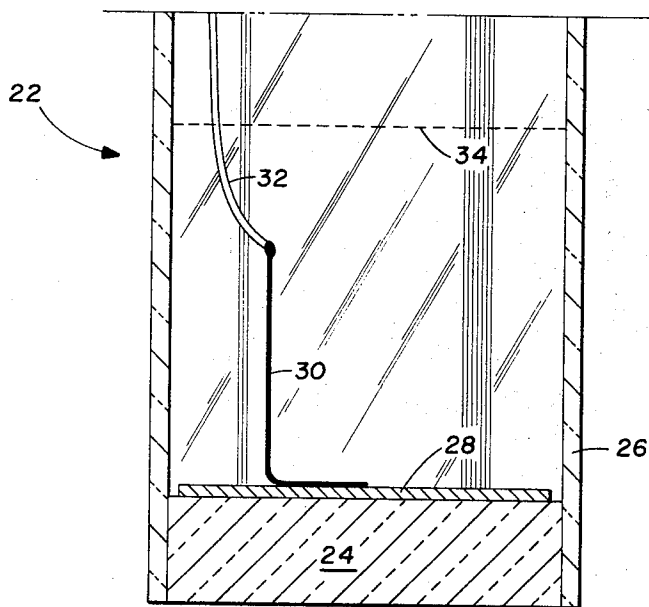
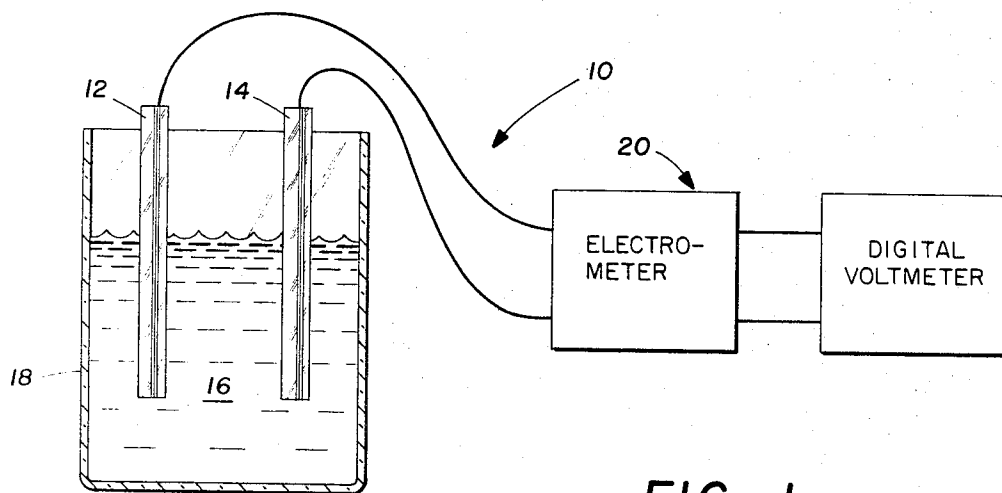
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**ABSTRACT**

A reference electrode and test electrode comprising a body of semi-conductor material having an element incorporated in it are positioned in a solution containing the element and the potential between the electrodes is measured. If the concentration of the element in the solution is known, the potential indicates the concentration of the element in the test electrode. Conversely, if the concentration in the test electrode is known, the potential indicates the concentration in the solution. In the latter case, the test electrode is prepared by plating a compound containing the element onto a body of semi-conductor material and diffusing the element into the body.

**8 Claims, 2 Drawing Figures**





INVENTOR

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## METHOD OF DETERMINING CONCENTRATIONS

This is a continuation of application Ser. No. 874,287, filed Nov. 5, 1969, now abandoned.

### BACKGROUND OF THE INVENTION

It is frequently desirable to know the concentration of specific elements in various substances. For example, during the manufacture of semi-conductor devices, it is often desirable to determine the concentration of various impurities in such materials as silicon, germanium, etc. Similarly, the determination of the concentration of various elements is a necessary part of such a diverse activities as manufacturing process control, pollution control, etc.

The measurement of the concentration of specific elements is greatly simplified by the use of ion selective electrodes. Such devices are responsive to ions of specific elements only and are typically employed in electrolytic cells including a reference electrode, an ion selective electrode, and an electrolyte. Since the ion selective electrode responds to ions of specific elements, the potential generated by such a cell is indicative of the concentration of those elements in the electrolyte.

Heretofore, most ion selective electrodes have had an effective range of about three orders of magnitude. This invention relates to an ion selective electrode having an effective range of up to seven orders of magnitude. The invention further relates to a method of determining a concentration of impurities in semi-conductor material such as silicon, germanium, etc.

### SUMMARY OF THE INVENTION

In accordance with the preferred embodiment, a potential indicative of the concentration of an element is generated by positioning a reference electrode and test electrode comprising a body of semi-conductor material having the element incorporated into it in a solution including the element. Preferably, either the concentration of the element in the solution is known, so that the potential is indicative of the concentration of the element in the body of semi-conductive material, or the concentration of the element in the body of semi-conductor material is known, so that the potential is indicative of the concentration of the element in the solution.

### DESCRIPTION OF THE DRAWING

A more complete understanding of the invention may be had by referring to the following Detailed Description when taken in conjunction with the drawing, wherein:

FIG. 1 is a schematic illustration of a concentration determining system employing the invention, and

FIG. 2 is an enlarged partial sectional view of a test electrode useful in the system shown in FIG. 1. DETAILED DESCRIPTION

Referring now to the drawing, and particularly to FIG. 1, a concentration determining system 10 employing the invention is shown. The system 10 includes a reference electrode 12 and a test electrode 14. The electrodes 12 and 14 are positioned in a quantity of liquid 16 which is contained in a beaker 18. The electrodes are connected to an electric potential indicating system 20 comprising an electrometer and a digital voltmeter.

The reference electrode 12 of the system 10 is conventional and may comprise any of the commercially available reference electrodes, such as silver-silver chloride electrode, etc. The potential indicating system 20 is also conventional and serves only to indicate the electric potential between the reference electrode 12 and the test electrode 14. The system 20 illustrated in FIG. 1 may be replaced by any of the other conventional potential indicating systems, if desired.

The test electrode 14 of the system 10 comprises a body of semi-conductor material having a particular element incorporated in it. The quantity of liquid 16 comprises a solution including ions of the same element. The system 10 may be employed to determine either the concentration of the element in the body of semi-conductor material or the concentration of the element in the solution. In either case, the potential indicating system 20 produces an output directly related to the concentration of the element.

By way of illustration, the concentration determining system 10 can be employed to measure the concentration of a particular impurity in a semi-conductor material. For example, the concentration of the impurity copper in a body of silicon can be measured by filling the beaker 18 of the system 10 with a solution containing a known concentration of copper and then employing the body of silicon as the test electrode 14. In such a case, the potential indicating system 20 produces an output indicative of the copper concentration in the body of silicon.

When the system 10 is employed to determine the concentration of an element in the body of liquid 16, a body of semi-conductor material including a known concentration of an element is employed as the test electrode 14. Such a test electrode 14 and the reference electrode 12 are inserted into a solution containing an unknown concentration of the element. In such a case, the potential indicating system 20 produces an output that is linearly related to the logarithm of the concentration of the element in the body of liquid.

It should be understood that the system 10 can be employed to determine unknown concentrations even though the concentration in the quantity of liquid 16 or in the test electrode 14 is not "known" in the literal sense. For example, assume that a test electrode 14 contains an unknown concentration of an element. If such an electrode is employed in a system of the type shown in FIG. 1 and if the beaker 18 of the system is sequentially filled with solutions containing different known concentrations of the element, a chart relating to the potential generated between the test electrode 14 and the reference electrode 12 to the concentration of the element in the quantity of liquid 16 can be prepared. Then, the chart and the test electrode can be employed to determine the concentration of the element in various solutions, even though the concentration of the element in the test electrode is not actually known.

Referring now to FIG. 2, there is shown an electrode structure 22 useful as the test electrode in the concentration determining system 10 when the system is used to determine the concentration of an element in a solution. The structure 22 includes an electrode 24 comprising a body of semi-conductor material having the element incorporated into it. The electrode 24 is mounted in a glass or plastic tube 26 and has a layer of gold 28 extending over it.

The layer of gold 28 on the electrode 24 is connected to a platinum wire 30, preferably by means of a coating of silver paint (not shown). The platinum wire 30 is in turn connected to a lead 32. The electrode 24 and the wire 30 are secured within the tube 26 by a quantity of epoxy (not shown) which preferably fills the tube 26 to a depth indicated by the dashed line 34.

The electrode 24 of the structure 22 is prepared by etching a body of semi-conductor material with an etching liquid including 15 parts by volume of a 49 percent solution of hydrofluoric acid in water, 10 parts of a 69 percent solution of nitric acid in water and five parts of a 99 percent solution of acetic acid in water. The body of semi-conductor material may be comprised in any of the commonly available semi-conductors. Preferably, however, a body of N-type silicon material is employed in the fabrication of the electrode.

After the body of semi-conductor material has been etched, it is placed in a plating solution comprised of one part by volume of a 49 percent solution of hydrofluoric acid in water, one part by volume of de-ionized water and a few grains of a compound including the particular element to which the electrode is to be sensitive. For example, if the concentration of copper is to be determined, a few grains of either copper sulfate or copper chloride are added to the hydrofluoric acid, de-ionized water solution. The interengagement of the semi-conductor body and the plating solution causes a layer of the element to plate onto the semi-conductor body by the process known as electroless plating.

When the plating of the element onto the body of semi-conductor material is complete, the element is incorporated into the semi-conductor material by thermal diffusion. This is preferably carried out by positioning the body of semi-conductor material in a quartz boat and then positioning the boat in a furnace. The furnace is purged for about 1 hour with helium after which the furnace is brought to a temperature of about 700°C and is held at that temperature for approximately 8 hours. During the heating operation, the helium within the furnace is maintained at a pressure of between 10 and 12 ounces per square inch.

When the thermal diffusion of the element into the semi-conductor material is completed, the body is removed from the furnace and is etched with the same etching solution that was employed prior to the plating step. The completed electrode is then ready for incorporation into an electrode structure of the type shown in FIG. 2. The completed structure comprises an ion selective electrode suitable for use in determining the concentration of the element that was incorporated into the body of semi-conductor material during the preparation of the electrode of the structure.

It has been found that by employing the ion selective electrode comprised of a body of semi-conductor material having an element incorporated in it as a test electrode, the sensitivity range of a concentration determining system is considerably increased. The test electrode shown in FIG. 2 is capable of determining molar concentrations between about  $10^{-8}$  M. and about  $10^{-1}$  M. That is, the electrode has a range of about seven orders of magnitude. Prior art ion sensitive electrodes typically have a range of about three orders of magnitude. Thus, electrodes constructed in accordance with the present invention have about twice the range of prior electrodes.

The various embodiments of the invention set forth herein primarily relate to determining the concentration of copper in semi-conductors and liquids. It will be understood, however, that the invention can be employed to determine the concentration of many elements in addition to copper. The only prerequisite to employing the invention to determine the concentration of a particular element is that the element be soluble in a semi-conductor material.

Although particular embodiments of the invention are illustrated in the drawing and described herein, it will be understood that the invention is not limited to the embodiments disclosed but is capable of rearrangement, modification and substitution of parts and elements without departing from the spirit of the invention.

What is claimed is:

1. In an electrolytic cell having a reference electrode, a semiconductor material containing an element of unknown concentration therein, and means for measuring voltage potential, the method of determining the concentration of said element contained in said semiconductor material including the steps of:

- a. dissolving a substance containing a known quantity of said element in said electrolytic cell to form a solution having a preselected concentration of ions of said element;
- b. forming a test electrode comprising said semiconductor material containing an unknown quantity of said element whose concentration is to be determined;
- c. positioning said reference electrode and said test electrode in the solution;
- d. measuring the potential between the reference electrode and the test electrode; and
- e. deriving the concentration of said element in said semiconductor material from said potential.

2. The method of determining the concentration of an element according to claim 1 wherein the element is present in the body of semi-conductor material as an impurity.

3. The method of determining an element according to claim 1 wherein the solution comprises an aqueous solution of the element.

4. The method of determining the concentration of an element according to claim 1 wherein the element is copper.

5. A method of determining the unknown concentration of an element in a compound comprising:

- a. forming a semiconductor electrode containing a known concentration of said element;
- b. providing a solution containing said element in unknown concentration in ionized form;
- c. immersing said semiconductor electrode and a reference electrode in the solution containing said element in ionized form;
- d. measuring the potential developed between said semiconductor electrode and said reference electrode; and
- e. deriving the concentration of said element in the solution containing said element from said potential.

6. The method of claim 1 wherein said semiconductor material is silicon.

7. The method of claim 5 wherein said semiconductor material is silicon.

8. The method of determining the concentration of an element according to claim 5 wherein the step of diffusing the element is carried out by coating the body of semi-conductor material with a compound including the element and then heating the coated body.

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