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V. J. VALVO

3,527,682

PROCESS FOR ELECTROLYTICALLY ETCHING INDIUM ANTIMONIDE

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FIG. 1a.

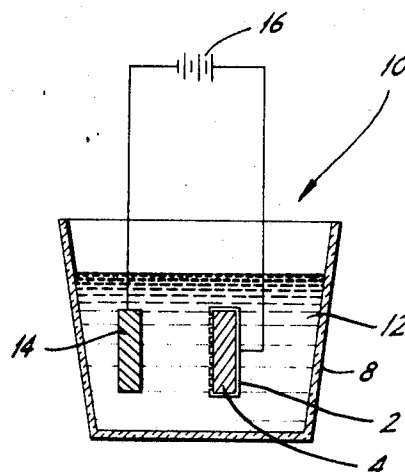
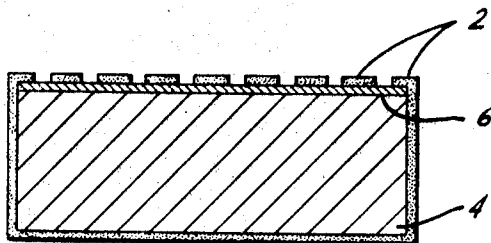


FIG. 2.

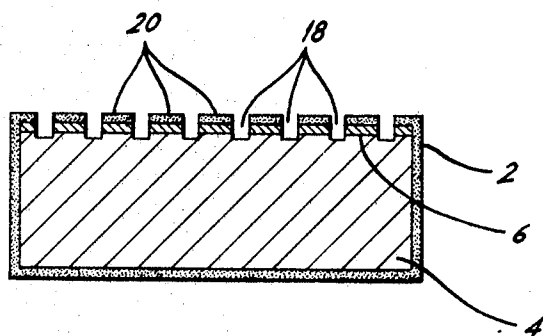


FIG. 1b.

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PROCESS FOR ELECTROLYTICALLY ETCHING INDIUM ANTIMONIDE

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7 Claims

ABSTRACT OF THE DISCLOSURE

Selected regions of an indium antimonide wafer are anodically etched by applying to those regions, via apertures in a mask placed on the wafer, a non-aqueous electrolyte which consists essentially of hydrochloric acid and ethylene glycol in the respective relative amounts of between two and ten cubic centimeters of hydrochloric acid per 100 cubic centimeters of ethylene glycol, and by applying between the wafer and the applied electrolyte a voltage poling the wafer positive with respect to the electrolyte and having a value high enough to produce anodic etching of the selected regions.

In the production of many semiconductor devices, such as mesa devices, it is necessary to form cuts or grooves in the semiconductor base material of the devices. Typically, electrolytic etching processes are used for this purpose.

Generally, electrolytic etching of the semiconductor base material is accomplished by coating those portions of the base material where no etching is desired with a resist (a material that is insoluble in the electrolyte to be used), immersing the coated base material in the electrolyte, and passing an electric current through the base material. The electric current oxidizes the uncoated portions of the base material and the oxidation products are carried off by the electrolyte. The coated portions of the base material are not etched because the resist prevents the electrolyte from contacting these portions.

It is evident that the straightness or definition of the cuts produced by electrolytic etching processes depends upon the adherence of the resist to the base material in the presence of the electrolyte. If the resist breaks down or becomes detached from the base material, the cuts will not have the desired definition.

Conventional electrolytes used for electrolytically etching intermetallic compound semiconductors, such as indium antimonide, generally contain nitric acid. Since conventional resists exhibit poor adherence to intermetallic compound semiconductors in the presence of nitric acid, electrolytes containing nitric acid can be used only for etching relatively gross devices with comparatively large spacings therebetween.

Accordingly, an object of the present invention is to provide an electrolyte which obviates the inherent disadvantages of the prior art.

A more specific object of the present invention is to provide a novel electrolyte which will produce high definition cuts in intermetallic compound semiconductors.

In accordance with the present invention, a solution of hydrochloric acid and ethylene glycol is used as the electrolyte in an electrolytic etching apparatus. In a preferred form of the present invention, the electrolyte contains between 2 and 10 cubic centimeters of hydrochloric acid for every 100 cubic centimeters of ethylene glycol.

These and other objects of the present invention will be more clearly understood when considered in conjunction with the accompanying drawings in which:

FIGS. 1a and 1b show sectional views of a semicon-

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ductor device at separate stages in the manufacture thereof in accordance with the present invention; and

FIG. 2 is a schematic representation of an apparatus suitable for the practice of the present invention.

For a better understanding of the present invention, the electrolyte of the present invention will be described in conjunction with the formation of a mesa array in an indium antimonide wafer. This array can be used as a photodetector.

As shown in FIG. 1a, preliminary to the etching, a coating 2 of an acid resist, such as Kodak photo resist, is applied to selected areas of an indium antimonide wafer 4 which has a shallow P-N junction 6 formed therein. The coating 2 and the junction 6 can be formed in any conventional manner.

The wafer, as thus treated, is supported by means (not shown) in a crucible 8 of a conventional electrolytic etching apparatus 10 (FIG. 2). Crucible 8, suitably of a dielectric material, contains an electrolyte 12, the composition of which will be explained in detail presently. Also supported in crucible 8 is an electrode 14 which is preferably of carbon. The electrolytic etching apparatus 10 further includes a DC power source 16, the positive terminal of which is connected through coating 2 to wafer 4 and the negative terminal of which is connected to electrode 14. For the etching of indium antimonide wafers, the optimum value of the output voltage of source 14 is 13 volts.

Referring again to electrolyte 12, it has been found that a solution composed of hydrochloric acid and ethylene glycol is a suitable electrolyte for etching intermetallic compound semiconductors, such as wafer 2. Preferably, the solution should contain between 2 and 10 cubic centimeters of hydrochloric acid for every 100 cubic centimeters of ethylene glycol. Ideally, the solution should contain 4 cubic centimeters of hydrochloric acid for every 100 cubic centimeters of ethylene glycol.

Connected as shown in FIG. 2, a constant current flows through the wafer 4. This current produces oxidation of the uncoated portions of wafer 4 and the oxidation products, in the form of positive ions, are transferred by the electrolyte 12 to the electrode 14. It is noted that the time for etching depends upon the volume of material to be etched. It is also noted that adequate etching of N-type conductivity semiconductor material may require the generation of additional holes in this material. This can be achieved by focusing additional light energy (not shown) upon the wafer 4.

After the desired amount of the wafer 4 has been etched, the wafer 4 is removed from the apparatus 10 for cleaning and further processing. As shown schematically in FIG. 1b, the processed wafer has a plurality of high resolution cuts 18 formed therein. These cuts define a plurality of mesas 20 in wafer 4.

Utilizing the electrolyte of the present invention, high resolution cuts 5 ten thousandths of an inch in width are obtainable. High resolution cuts of such small width are not obtainable with prior art electrolytes.

Although the invention has been described in conjunction with the etching of indium antimonide, the electrolyte can also be used to etch other intermetallic semiconductor compounds. While the invention has been described in conjunction with the formation of mesas, it will be apparent that other uses of the electrolyte of the present invention will occur to those skilled in the art within the scope of the invention. Accordingly, I desire the scope of my invention to be limited only by the appended claims.

I claim:

1. In a process for electrolytically etching at least one selected region of the surface of a body of indium antimonide, comprising the steps of

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applying an electrolyte to said selected region, and applying between said electrolyte and said selected region a voltage establishing said selected region at a potential positive with respect to the potential of said electrolyte and having a magnitude high enough to produce anodic etching of said selected region, the improvement wherein said electrolyte is a non-aqueous solution consisting essentially of ethylene glycol and hydrochloric acid, said hydrochloric acid having a concentration of between two and ten cubic centimeters per one hundred cubic centimeters of said ethylene glycol.

2. A process according to claim 1, comprising the additional step, performed before said step of applying said electrolyte, of placing on said surface of said body a mask which has, over each of said selected surface regions, an aperture exposing said selected region, thereby to permit said electrolyte, when applied, to contact said selected region, and which covers other regions of said surface, thereby to prevent said electrolyte when applied from contacting said other regions.

3. A process according to claim 2, in which said mask is composed of an acid resist.

4. In a process for producing at least two physically separated portions of a given conductivity type of a wafer of semiconductive indium antimonide comprising a major surface, a first region of said given conductivity type bounded respectively by said major surface and another surface within said wafer and a second region of conductivity type opposite said given type also bounded by said other surface and exclusive of said first region, by selectively etching through an apertured mask those parts of said wafer which lie between said two portions and are bounded by said major surface and a surface wholly within said second region,

the improvement wherein said etching step comprises applying to said parts, by way of said apertures, a

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non-aqueous electrolyte consisting essentially of ethylene glycol and hydrochloric acid, said hydrochloric acid having a concentration of between two and ten cubic centimeters per one hundred cubic centimeters of said ethylene glycol, applying between said parts and said electrolyte a voltage establishing said parts at a potential positive with respect to the potential of said solution and having a value high enough to produce anodic etching of said parts, and continuing said voltage application until said parts have been removed by said anodic etching.

5. A process according to claim 4, in which said mask is composed of an acid resist.

6. A process according to claim 4 in which said mask covers all surface portions of said wafer which are not to be etched, said electrolyte is applied to said parts to be etched by immersing said wafer in said electrolyte, and said voltage is applied between said wafer and a cathode immersed in said electrolyte in spaced relation to said wafer.

7. A process according to claim 6, in which said mask is composed of an acid resist.

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ROBERT K. MIHALEK, Primary Examiner

U.S. Cl. X.R.

204—141

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,527,682 Dated September 8, 1970

Inventor(s) Vincent J. Valvo

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Claim 4, line 25, "of a wafer" should be -- in a wafer --.

SIGNED AND
SEALED
NOV 3 1970

(SEAL)

Attest:

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