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PROCESS FOR ELECTROLYTICALLY ETCHING INDIUM ARSENIDE

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ABSTRACT OF THE DISCLOSURE

A nitric acid-ethylene glycol bath is utilized to electrolytically etch indium arsenide crystals. The etched crystals are useful as semiconductor elements.

If indium arsenide crystals are to be used as semiconductor devices, e.g. a Hall element or a laser, the surface of the crystals must be free from damage, smooth, and chemically clean. It is known to treat the crystals by chemical etching and by electrolytic etching. Ordinarily, chemical etching is effected after mechanical lapping. However, it is difficult to obtain a smooth and clean surface with this procedure since there are formed etch pits which are derived from surface strains due to mechanical lapping, and from lattice defects such as dislocation, twin (compound crystal formation) and grain boundary of crystals.

In prior art electrolytic etching processes, it has been proposed to utilize a perchloric acid and acetic acid bath, and a potassium ferrocyanide and potassium hydroxide bath. However, such baths have the disadvantages that oxide films are formed on the crystal surfaces, and the reagents are dangerous to handle.

The present invention overcomes the above mentioned disadvantages of the prior art by utilizing an electrolytic etching bath consisting of a mixture of one volume of concentrated nitric acid with one-three volumes of ethylene glycol. In this mixture, the nitric acid concentration is substantially lowered to facilitate control of the etching rate, and the use of this bath makes it possible to obtain a glossy, smooth and clear surface without forming an oxide film on the surface of the crystal.

The reagents employed in the etching bath of the present invention are inexpensive, and their handling characteristics compare favorably with those of reagents used in prior art baths. Also, the preparation of the electrolytic etching bath of the invention is quite simple.

The etching bath of the present invention which is used to prepare indium arsenide crystals for use in semiconductor elements is prepared by adding to 98% nitric acid, 1–3 times the volume of the nitric acid of ethylene glycol. In the present invention, the volume ratio of nitric acid to ethylene glycol is within the range of about 1:1 to 1:3 since when the volume ratio is more than about 1:1, i.e. when there is more nitric acid than ethylene glycol, an oxide film is formed on the surface of the indium arsenide during the electrolytic etching. When the volume ratio is less than about 1:3, the current density in the etching bath is lowered, and etch pits are formed on the surface of the crystals due to dislocation or twin.

The electrolytic etching is carried out at a current density of 1.0–5.0 a./cm.^{2} and a bath temperature of 20–40° C. An indium arsenide crystal fragment which has been mechanically lapped on its surface with a polishing material such as aluminum oxide or silicon carbide of 10 microns diameter is used as an anode in an electrical circuit which includes a platinum plate cathode.

The current density is maintained within the range of 1.0–5.0 a./cm.^{2} because if the current density is lower than about 1.0 a./cm.^{2}, etch pits resulting from surface strains or dislocation are formed over the surface of the crystal. At current densities higher than about 5.0 a./cm.^{2}, a thin oxide film is formed on the surface of the crystal.

The invention will be further illustrated by way of the following examples.

Example 1

Electrolytic bath composition
Nitric acid ---------- 1 part by volume.
Ethylene glycol ---------- 1 part by volume.
Bath temperature ---------- 25° C.
Current density ---------- 3.5 a./cm.^{2}

In the above mentioned electrolytic etching bath, an indium arsenide crystal fragment mechanically lapped on the surface with an aluminum oxide polishing material of 10μ in diameter was electrolytically etched at the above mentioned temperature and current density, using said fragment as an anode and a platinum plate as a cathode, to obtain a smooth and clean mirror surface. The electrolytically etched surface was observed with an optical microscope and was free from etch pits due to dislocation, twin and grain boundary.

Example 2

Electrolytic bath composition
Nitric acid ---------- 1 part by volume.
Ethylene glycol ---------- 3 parts by volume.
Bath temperature ---------- 35° C.
Current density ---------- 4.5 a./cm.^{2}

In the above mentioned electrolytic etching bath, an indium arsenide crystal fragment mechanically lapped on the surface with an aluminum oxide polishing material of 10μ in diameter was electrolytically etched at the above mentioned bath temperature and current density, using said fragment as an anode and a platinum plate as a cathode, to obtain a smooth and clean mirror surface. The electrolytically etched surface was observed with an optical microscope and was free from etch pits due to dislocation, twin and grain boundary.

What is claimed is:

1. A process for electrically etching indium arsenide, comprising introducing an indium arsenide crystal into a substantially nonaqueous bath consisting essentially of one part by volume of nitric said and about 1 to 3 parts by volume of ethylene glycol and electrolytically etching said crystal while employed as an anode in an electric circuit to obtain a smooth and clear mirror surface.

2. A process according to claim 1, wherein the electrolytic etching step is carried out at a current density of about 1.0–5.0 a./cm.^{2}.

3. A process according to claim 1, wherein the temperature of the bath is maintained at about 20–40° C. during the electrolytic etching step.

References Cited

FOREIGN PATENTS

602,880 8/1960 Canada.

OTHER REFERENCES

J. F. Dewald: J. Electro Chem. Soc. 104, 244 (1957).

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