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3,764,424

FABRICATION OF GALLIUM ARSENIDE DEVICES

Filed May 3, 1971

FIG. 1

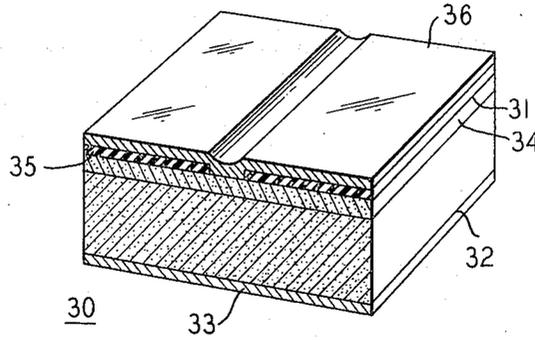


FIG. 2 A

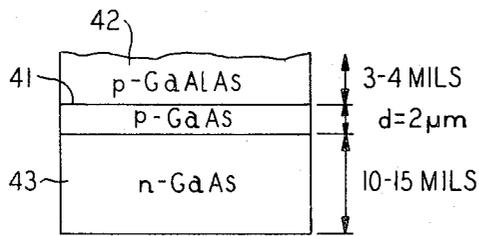


FIG. 2 B

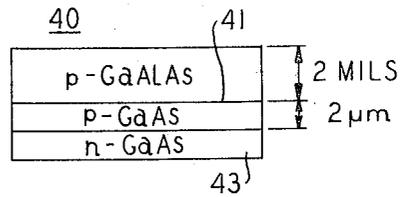
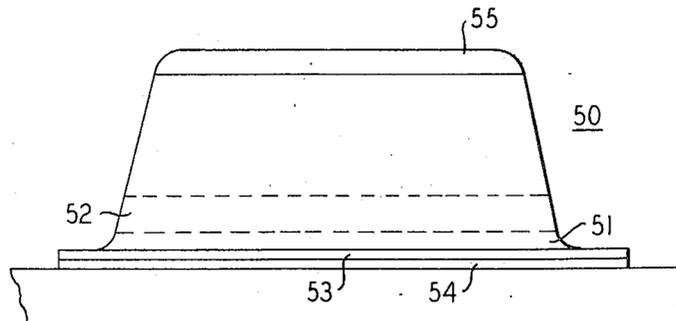


FIG. 3



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3,764,424

FABRICATION OF GALLIUM ARSENIDE DEVICES
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6 Claims

ABSTRACT OF THE DISCLOSURE

A process is described for the fabrication of gallium arsenide devices in which chemical polishing is carried out on the (111) Ga-rich surface using a pH adjusted peroxide polishing solution. This polishing agent produces particularly high quality surfaces which is difficult to achieve on the (111) Ga-rich face using conventional polishing agents.

BACKGROUND OF THE INVENTION

(1) Field of the invention

The invention relates to a process for the fabrication of gallium arsenide devices. In particular, it relates to polishing surfaces of gallium arsenide including the (111) Ga-rich face.

(2) Description of the prior art

In the fabrication of gallium arsenide devices polishing of surfaces is often required. In relatively crude devices abrasive polishes, such as diamond paste, have often proved satisfactory. However, as more sophisticated devices were made, it became apparent that abrasive polishing was unsatisfactory for many reasons. For example, the surface was often left in a highly strained condition which sometimes had deleterious effects on device performance. For this reason extensive efforts were made to develop a chemical polishing agent in which material was removed by chemical reaction rather than abrasion.

Some time ago Sullivan and Kolb (J. Electrochem. Soc., 110, 585 (1963)) described a polishing solution containing bromine and methanol. This polishing agent was a considerable improvement over abrasive polishing and is now used extensively in the fabrication of gallium arsenide devices such as optical lasers, transistors and diodes.

The further development of gallium arsenide devices has led to the requirement, at least in some instances, of polished surfaces of higher and higher quality. The polishing process using the bromine-methanol solution continues to be used satisfactorily even in these instances, although in the case of polishing the (111) Ga-rich surface of gallium arsenide polished surfaces of high quality sometimes requires the use of more dilute bromine-methanol solution. This leads to increased polishing time.

SUMMARY OF THE INVENTION

The invention is a process for the fabrication of gallium arsenide devices in which pH adjusted peroxide solution is used as a chemical polishing agent for polishing Ga-rich (111) surface and other surfaces of gallium arsenide. This chemical polishing agent yields surfaces of high optical quality including the (111) Ga-rich surface of surfaces is often required. In relatively crude devices typically adjusted with ammonium hydroxide, but other alkaline substances as, for example, sodium hydroxide and potassium hydroxide, have been used. The pH of the peroxide solution is between 5 and 10. A pH between 6 and 8 is preferred. The polishing agent is also used in devices containing substituted gallium arsenide such as gallium aluminum arsenide. This process is used to fabricate a variety of gallium arsenide devices including junction lasers.

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BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a perspective view of a gallium arsenide laser structure made using the inventive process;

FIG. 2 is a side view of a gallium arsenide device with a heterojunction fabricated using the inventive process; and
FIG. 3 is a side view of a high-frequency gallium arsenide diode fabricated by the inventive process.

DETAILED DESCRIPTION

(1) Introduction

The invention is a process for the fabrication of gallium arsenide devices. This process involves the use of peroxide solutions for the preparation of gallium arsenide surfaces. The pH of the peroxide may be adjusted by the addition of a suitable agent. Particular importance is placed on obtaining good optical polishes on the (111) Ga-rich surface of gallium arsenide, although other surfaces of this crystal may also be involved in the preparation. This surface preparation may involve uniform removal of material as in optical polishing or preparation of the surface for epitaxial crystal growth.

In the preparation of gallium arsenide crystals for use in various devices it is often required to obtain an optical polish of high quality on the (111) Ga-rich surface. This requirement might arise, for example, because of the shape of the gallium arsenide crystal available or because of some desirable property of the (111) surface such as suitability for epitaxial crystal growth. The pH adjusted peroxide solution is particularly suitable for surface preparation in these instances since it produces in reasonable times surfaces of high optical quality which do meet device requirements. Also, surfaces of good optical quality can be produced in all crystallographic orientations of the gallium arsenide so that the same polishing agent can be used for preparing all surfaces required in the device fabrication. Other device requirements are also met using this polishing agent. For example, good ohmic electrical contact is achieved on the polished surface and residual surface strains are minimal.

(2) Evaluation of the process

In order to evaluate the characteristics of the buffered peroxide solution as a polishing agent for gallium arsenide several polishing experiments were carried out. The apparatus used in these experiments was of conventional design. It consists of a suitably coated turntable and several interchangeable flat plates. These plates can be used with any desired polishing cloth or alternatively without a cloth during lapping operations. In the polishing operation, the surface of gallium arsenide being polished is rubbed or wiped to remove the surface layer formed from the reaction of polishing solution with gallium arsenide.

Polishing agents had the following compositions. The peroxide solution contained 1 ml. ammonium hydroxide and 700 ml. of 30 percent peroxide. The bromide-methanol solution was made up of 1 ml. bromine and 2,000 ml. methanol. The polishing solutions were applied at rates of 800-1400 ml. per hr. Polishing was usually continued until about 500 microns of material had been removed.

Polishing experiments were carried out on the (100), (111) Ga-rich and (111) As-rich faces of gallium arsenide. The pH adjusted peroxide solutions yielded surfaces with good optical polish on all faces. The polishing rate for the peroxide solution was initially about 24 microns per hour but decreased to about 17 microns per hour after about an hour and thereafter remained approximately constant. The bromine-methanol solution yielded surfaces of good optical quality on the (100) and (111) As-rich faces of gallium arsenide. Good results were also obtained on the (111) Ga-rich surface using a more dilute bromine-methanol solution. However, the

polishing rate was slower and a longer time was required to polish the surface.

(3) Composition of the polishing agent

The polishing agent has a peroxide concentration between 3 and 50 percent by weight. Polishing solutions with peroxide concentrations below 3 percent exhibit an inconveniently slow polishing rate. Above 50 percent by weight the solutions become difficult to handle because of instability. The preferred concentration of 25-35 percent by weight arises largely as a matter of convenience. This composition is readily available and easily handled. The pH of the solution should be between 5 and 10. Outside this range surfaces of high optical quality are no longer obtained. A pH from 6 to 8 is preferred as yielding the best results. The pH is adjusted by any convenient alkaline agent. Ammonia is particularly convenient because it can be obtained in relatively pure form and does not leave a residue on evaporation. However, other alkaline agents such as, for example, KOH or NaOH, may be used.

(4) Semiconductor devices

FIG. 1 shows a typical device produced by the inventive process. The fabrication of the laser structure 30 begins with a piece of n-type gallium arsenide. Top 31 and bottom 32 faces are polished using the buffered peroxide polishing agent. A metal electrode 33 is then put on one face so as to form an ohmic electrical contact. Zinc or other suitable metal is then diffused into the other face 31 so as to form a p-junction 34. An oxide layer 35 of prescribed geometry is then put down on the p-junction 34 and a metal electrode 36 put down on top of this layer.

FIG. 2 shows a type of semiconductor device 40 which requires precise polishing techniques for fabrication. Again, fabrication is begun with a piece of n-type gallium arsenide. One of the surfaces is polished using the inventive process. Zinc or other suitable metal is then diffused into this surface 41. This produces a thin layer of p-type gallium arsenide with a thickness of approximately 2 microns. Then p-type aluminum substituted gallium arsenide is deposited on the surface of the p-type gallium arsenide to form a heterojunction and this surface 42 is polished flat using the inventive process. Then large amounts of the n-type gallium arsenide must be removed so that only a thin layer 43 of n-type material remains. On application of electrodes, this structure is used as an electroluminescent diode.

FIG. 3 is a side view of a gallium arsenide microwave diode 50 made by the inventive process. A typical diode consists of an outer epitaxial layer 51 with an electron concentration of $6 \times 10^{15} \text{ cm.}^{-3}$, and 8 micron thick inner buffer layer 52, with an electron density of $5 \times 10^{17} \text{ cm.}^{-3}$.

A platinum 53 and gold 54 layer are attached to the epitaxial layer 51. A gold-plated back contact 55 is attached to the top of the diode. The inventive process is involved in the attachment of all of these layers.

What is claimed is:

1. A process for the fabrication of a gallium arsenide device comprising the preparation of gallium arsenide surfaces including the (111) Ga-rich surface comprising the steps of:

- (a) wetting the surface being polished with an aqueous solution of a chemical polishing agent;
- (b) exposing the surface to mechanical abrasion;

characterized in that the aqueous solution consists essentially of between 3 and 50 percent by weight hydrogen peroxide and the pH of the aqueous solution is between 5 and 10.

2. The process of claim 1 in which the peroxide concentration is between 25 and 35 percent by weight.

3. The process of claim 1 in which the pH of the aqueous solution of chemical polishing agent is between 6 and 8.

4. The process of claim 1 in which the pH of the aqueous solution of the chemical polishing agent is adjusted with ammonia.

5. The process of claim 1 in which the pH of the aqueous solution of the chemical polishing agent is adjusted with sodium hydroxide.

6. The process of claim 1 in which the pH of the aqueous solution is the chemical polishing agent is adjusted with potassium hydroxide.

References Cited

UNITED STATES PATENTS

Evaluation of a New Polish for GaAs Using a Peroxide-Alkaline Solution, Dymant et al., vol. 117, No. 11, November 1970 *Electrochemical Society Rev. & News*, p. 405 C; same title as above by Dymant et al., *J. of Electrochem. Soc.*, *Solid State Science*, August 1971, pp. 1346-50; On p. 1350, *Manuscript Recd. Nov. 30, 1970*.

Detect Structure of GaPa Etc. by Saul, J. of *Electrochem. Soc.*, *Solid State Science*, November 1968, pp. 1184-1190, see p. 1185 *Etchart #4*.

Selective Etchg. of GaAs in $\text{H}_2\text{SO}_4\text{-H}_2\text{O}_2\text{-H}_2\text{O}$ System, Iida et al., *J. of Electrochem. Soc.*, vol. 18, No. 5 May 1971, *Manuscript Recd. July 30, 1970*.

JACOB H. STEINBERG, Primary Examiner

U.S. Cl. X.R.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,764,424 Dated October 9, 1973

Inventor(s) Augustus Julius Sayko

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

Column 1, line 43, after "used" insert --quite--;

line 63, after "of" insert

--gallium arsenide.--,

delete "surfaces is often required.

In relatively crude devices" and

substitute --The pH of the polishing

solution is--.

Column 2, line 31, change "reasonabe" to --reasonable--.

Column 4, line 29, change "is" to --of--.

Signed and sealed this 26th day of March 1974.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents