United States Patent

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[54] **PREPARATION OF III–V ALLOYS FOR INFRARED DETECTORS**
9 Claims, No Drawings

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[56] **References Cited**
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3,558,373 1/1971 Moody et al. 148/171

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ABSTRACT: A single crystal InAs–InSb alloy is prepared on a III–V substrate by flash evaporation of a mixture of granulated InAs and InSb in a vacuum system, subsequent condensation and solidification of the vapor on the substrate and subsequent annealing. The flash evaporation and solidification is thus followed by suitable annealing of the deposited material for several weeks at a temperature close to but below the solidus temperature of the alloy. Prior to annealing, an oxide film may be formed on the deposited alloy to prevent loss of the more volatile constituents.

PREPARATION OF III–V ALLOYS FOR INFRARED DETECTORS

BACKGROUND

The invention relates to the production of semiconductor materials, and more particularly relates to the production of single crystal III–V alloys for use in infrared detecting devices.

Various group III–V compounds have been found to have properties which, for some applications, are superior to those of the group IV semiconductor materials. These compounds offer a wide range of energy gaps. InAs and InSb have been found to offer energy gaps particularly suitable in the infrared region of the electromagnetic spectrum. Several methods are currently known for preparing homogeneous alloys of various III–V compounds. A few methods, such as chemical vapor deposition, have been used to form single crystal alloys of some of these materials. Little, however, is currently known about the formation of single crystal alloys of InAs–InSb. Single crystals are of course necessary for use in electronic devices.

The flash evaporation technique for depositing mixtures of the III–V compounds on a suitable substrate has been described in several technical papers. For example, E. K. Muller and J. L. Richards describe such a technique in an article entitled "Miscibility of III–V Semiconductors Studied by Flash Evaporation" which is found in the Apr. 1964 *Journal of Applied Physics*, Vol. 35, No. 4. The Muller and Richards technique, however, when used with the pseudobinary InAs–InSb system produces a homogenous solid alloy which is not single crystal. In their conventional flash evaporation process, a powder of fine grains is fed continuously onto a heated evaporator which is hot enough to vaporize all of the constituents. As each grain strikes the evaporator, a vapor is produced which diffuses toward a substrate held at a small distance from the evaporator. The substrate is maintained at temperature sufficiently low to condense all the constituents of the vapor including the most volatile ones. A film of the desired alloy condenses on the substrate and the film has approximately the same composition as the initial powder because the powder delivery rate is made sufficiently fast to negate the effect of some elements evaporating more rapidly than others as explained by Muller and Richards. Although a homogeneous alloy is deposited, it is not single crystal.

Various types of annealing processes have been performed in the semiconductor fabrication art. Finely ground powders have been very tightly compressed and annealed for periods extending anywhere from several weeks to several months. Such annealing, however, requires extensive periods of time thereby making conventional annealing substantially impractical and commercially undesirable for the manufacture of devices. Although the annealing of fine compressed powders of InAs and InSb has produced ingots with homogeneous regions, the ingots themselves were not homogeneous. Furthermore, such ingots were polycrystalline.

In an attempt to fabricate alloys of InAs–InSb zone recrystallization, similar to zone refining, has been used but, while producing ingots with homogeneous regions, produces an overall polycrystalline ingot. Similarly, directional freezing has been used but it too produces polycrystalline ingots.

It is therefore an object of the invention to provide a method for fabricating single crystal alloys of two or more III–V compounds.

Another object of the invention is to provide a method for fabricating single crystal allows of InAs and InSb which method can be performed in a commercially feasible short period of time.

Further objects and features of the invention will be apparent from the following specification and claims.

SUMMARY OF THE INVENTION

We have found that the foregoing and other objects may be attained by a method for preparing a single crystal III–V alloy on a suitable substrate, the method comprising: (a) effecting the vaporization of the compounds which are the constituents of the III–V alloy to provide a vapor mixture; (b) depositing the III–V alloy on the substrate by condensation and solidification of the vapor mixture; and (c) annealing the deposited alloy until a suitably large area single crystal is formed.

The method is more effective if a mixture of InAs particles and InSb particles are impinged upon a heated surface which surface is heated above the melting point of the particles thereby vaporizing the particles and so that a homogenous alloy therefrom is deposited on a substrate which is maintained at a suitably low temperature for effecting condensation of the vapor. Annealing is preferably done immediately below the solidus line.

DETAILED DESCRIPTION

The flash evaporation apparatus used in this invention is contained within an enclosure which can be evacuated prior to its operation. A hopper is mounted within the enclosure for containing a powder mixture of the desired constituents. In the preferred embodiment, the hopper is initially filled with a finely powdered mixture of InSb and InAs. This mixture has a proportional composition approximately the same as that desired in the ultimate single crystal to be formed. A boat, preferably a tantalum boat, is mounted in the enclosure beneath the hopper so that the powder may be continuously fed from the hopper onto the boat. The boat is provided with means for heating it to a sufficient temperature. The boat temperature must be high enough to quickly evaporate the least volatile constituent of the mixed powder as the grains fall and impinge upon the boat. For the preferred InAs–InSb powder, a temperature above 1,500° C. would be desired. A vibrating or other feeder is provided to continuously feed the powdered mixture from the hopper to the boat at a desired feed rate.

A substrate holder capable of being heated to a controlled temperature is positioned above the tantalum boat. I have positioned the heater 10 centimeters above the boat. A cleaned and etched III–V substrate is mounted to the substrate holder. During operation, the substrate will be maintained at a temperature sufficiently low to prevent re-vaporization or decomposition of the more volatile constituents. With the preferred constituents, the temperature of the substrate holder may be held preferably below 405° C.

The preferred embodiment of my method begins by evacuating the enclosure preferably to a pressure below 10^{-} Torr. The tantalum boat is heated to a temperature high enough to evaporate the least volatile constituents. The substrate is brought to its condensation temperature. The vibrating trough or other means is then energized to begin feeding a continuous stream from the hopper on to the tantalum boat. As the particles strike the boat, they are vaporized and the vapor diffuses through the enclosure. The substrate placed in the vapor stream issuing from the boat becomes immersed in the vapor and, because of its temperature, is a favorable site on which the vapor is condensed and solidified. The alloy deposited in this manner is homogeneous though not (except at a temperature within a very narrow range) a single crystal. For example, with a mixture of 60 mol percent indium antimonide and the balance indium arsenide, the resultant film composition will be at least 56 mol percent indium antimonide and the balance indium arsenide for a substrate maintained at a temperature between 350° and 405° C. If the substrate is held at a range of temperature between 390° and 405° C. a single crystal may be formed even without annealing. I prefer to hold the substrate at a temperature between 398° and 400° C.

Following the deposition of a sufficiently thick film of the homogeneous alloy, the apparatus is cooled and a thin protective film is formed on the surface of the alloy to prevent loss of the more volatile constituents. I used an oxide film which was 1,000 angstroms thick but small variations therein are of course possible. This film is desirable because of the annealing temperature used as explained below.

The homogeneous polycrystalline alloy film is then preferably annealed at a temperature below, but preferably close to, the solidus temperature for the alloy deposited. Because annealing is done so close to the solidus temperature, the thin oxide film is needed to prevent loss of the more volatile constituent of the alloy. Good quality single crystals can be formed by annealing at such a temperature for a period of a few weeks rather than a few months. Of course, the exact anneal time and temperature will depend upon the constituents, the proportional composition, and the quality of the crystals desired.

It is obvious that a great variety of proportional compositions, temperatures, and constituents may be used in performing the process of my invention. I may use mixtures of indium arsenide and indium antimonide over a fairly broad range of proportions. I may use 80 mol percent indium arsenide with the remainder indium antimonide, and I may vary the proportions of indium arsenide at any proportion between 80 mol percent to 40 mol percent, as for example to 70 mol percent, 60 mol percent, 50 mol percent, 46 mol percent, 44 mol percent, 42 mol percent and 40 mol percent, providing in each case indium antimonide for the balance of the mixture.

I may provide a temperature of the tantalum boat at 1,000° C. but we prefer that the temperature be maintained at 1,500° C. or above.

The substrate may be held at a temperature of 300° to 405° C., securing crystalline material in certain cases without annealing. The following examples illustrate the process and the composition of the invention using particular materials, steps, and conditions. It is to be understood that these examples are furnished by way of illustration and are not intended to be by way of limitation.

EXAMPLE I

InSb was ground into a powder and InAs was ground into a powder and formed into a mixture having 44.0 mol percent InSb and the balance InAs. This mixture was continuously fed onto a tantalum boat above 1,500° C. The substrate was held at 350° C. and a homogeneous alloy film was formed thereon. An oxide film 1,000 angstroms thick was formed on the surface and the substrate with its film was annealed at 555° C. for 3 weeks. Examination using Laue X-ray back reflection techniques indicated that the alloys were single crystal.

EXAMPLE II

InSb was ground into a powder and InAs was ground into a powder and formed into a mixture having a 60 mol percent InSb content. This mixture was continuously fed onto a tantalum boat above 1,500° C. The substrate was held at 350° C. and a homogeneous alloy film was formed thereon. An oxide film 1,000 angstroms thick was formed on the surface and the substrate with its film was annealed at 535° C. for 4 weeks. Examination using Laue X-ray reflection techniques indicated that the alloy were single crystal.

Thus, in general, the method of the invention is performed by first effecting the vaporization of the intended constituents of the alloy in order to provide a vapor mixture of these constituents. A substrate immersed in this vapor provides a suitable site for the deposition of the III–V alloy vapor by condensation and solidification. The deposited film is then preferably annealed below the solidus temperature until a suitably large area of single crystal is formed.

The preferred method for effecting the vaporization is to impinge particles of one of the constituent III–V compounds upon a heated surface which is heated sufficiently high to cause practically instantaneous vaporization of the particles Simultaneously, particles of the other constituent III–V compound are impinged on a surface heated hot enough to vaporize that compound. I have found it preferable to use a single heated surface, heated above the melting point of the least volatile constituent and to impinge the particles on the surface in the same proportion as that desired in the single crystal III–V alloy.

It is also desirable to form a thin protective film on the surface of the deposited alloy after depositing the alloy on the substrate but prior to annealing the alloy. We have used oxides for this purpose and particularly silicon oxide.

It is to be understood that while the specific examples given describe preferred embodiments of my invention, they are for the purposes of illustration only, that the method of the invention is not limited to the precise details and conditions disclosed, and that various changes may be made therein without departing from the spirit of the invention which is defined by the following claims.

I claim:

1. A method for preparing a single crystal III–V pseudobinary alloy on a substrate, the method comprising in order:

a. effecting the vaporization of the compounds which are the intended constituents of said alloy to provide a vapor mixture;

b. depositing a III–V alloy on the substrate by condensation and solidification of said vapor mixture on the substrate; and

c. annealing the deposited alloy until a suitably large area single crystal is formed.

2. A method according to claim **1**, wherein said vaporization is effected by:

a. impinging particles of a constituent III–V compound on a heated surface to vaporize them, the surface being heated to a temperature above the melting point of the particles impinged thereon; and

b. simultaneously impinging particles of another constituent III–V compound on a heated surface to vaporize them, the surface being heated to a temperature above the melting point of the particles impinging thereon.

3. A method according to claim **2**, wherein the particles are impinged on the same surface in proportions approximating the proportions desired in said single crystal III–V alloy.

4. A method according to claim **3**, wherein said constituents comprise InSb and InAs, the substrate is maintained at a temperature below 405° C. during said depositing step, and said heated surface is maintained at a temperature above 1,500° C. during said vaporization.

5. A method according to claim **4**, wherein the constituents are 44 mole percent InSb and the balance InAs, the annealing period is approximately 3 weeks, and the annealing temperature is approximately 555° C.

6. A method according to claim **1**, wherein after said depositing, but prior to said annealing, a film is formed on the surface of the deposited alloy.

7. A method according to claim **6**, wherein the film is a silicon oxide film.

8. A method according to claim **7**, wherein the constituents are 44 mol percent InSb and the balance InAs, the substrate is maintained at a temperature below 400° C. during said depositing step, the vaporization is effected by impinging the particles of the constituent III–V compounds on a heated surface maintained at a temperature above 1,500° C. to effect vaporization thereof, and the annealing is effected by maintaining the deposited alloy at a temperature of approximately 555° C. for a period of approximately 3 weeks.

9. A method according to claim **7**, wherein the constituents are 60 mol percent indium antimonide and the balance indium arsenide.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,634,143 Dated January 11, 1972

Inventor(s) Leo C. Brennan

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 30 should read ... produces a homogeneous solid alloy...;

Column 2, lines 9-10 should read ...so that a homogeneous alloy therefrom is...;

Column 2, lines 46-47 should read ... to a pressure below $\underline{10^{-6}}$ Torr. ...;

Column 2, line 54 should read ...vapor diffuses throughout the enclosure. ...;

Column 3, line 55 should read ...the alloys were single crystal. ...;

Column 3, lines 67-68 should read ...vaporization of the particles. Simultaneously, ...

Signed and sealed this 1st day of August 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents