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Gramann

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[54] **APPARATUS FOR LIQUID PHASE EPITAXY**

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Related U.S. Application Data

[62] Division of Ser. No. 67,534, Aug. 27, 1970, abandoned.

[30] **Foreign Application Priority Data**

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Sept. 11, 1969 Germany 6935720

[52] **U.S. Cl.** **118/421,** 148/171
[51] **Int. Cl.** **H01l 7/00**
[58] **Field of Search** 118/421, 415; 117/201; 148/171, 172, 173

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[57] **ABSTRACT**

Apparatus for liquid phase exitaxy includes a refractory tubular vessel rotatable about it longitudinal axis and supportive of a substrate on an upper wall. A crucible is longitudinally movable from a position external to a confining wall of the vessel, whereby to be charged, to a position whereby to be sealed by said wall. Means rotate the vessel 180° and effect further inward movement of the crucible whereby to effect contact between the substrate and growth material.

5 Claims, 10 Drawing Figures

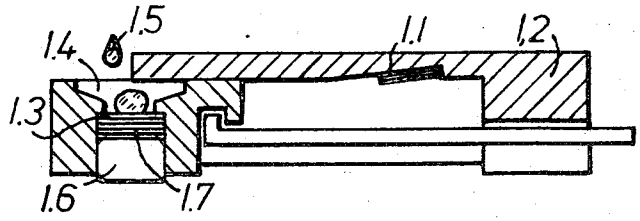


Fig.1

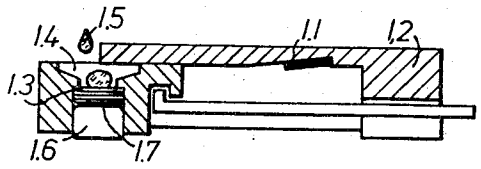


Fig.2

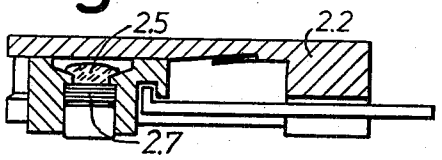


Fig.3

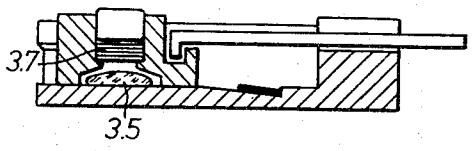


Fig.4

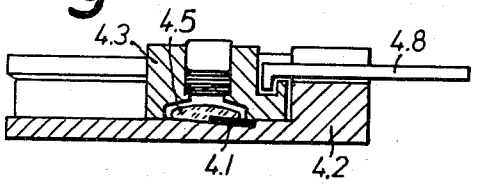


Fig.5

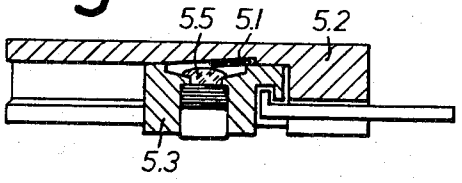


Fig.6

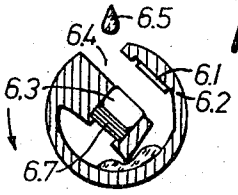


Fig.7

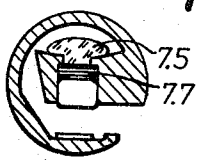


Fig.8

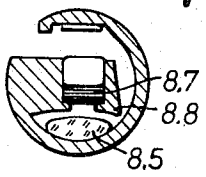


Fig.9

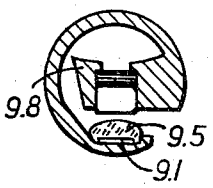
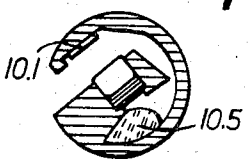


Fig.10



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APPARATUS FOR LIQUID PHASE EPITAXY

CROSS REFERENCE TO RELATED APPLICATION

This application is a division of Application Ser. No. 67,534, filed Aug. 27, 1970 now abandoned.

BACKGROUND OF THE INVENTION

The invention relates to a method and apparatus for liquid-phase epitaxy, particularly of binary systems.

Such systems, for example compounds of the third and fifth group of the periodic system of elements such as gallium arsenide, pay an important part in electrical engineering because of their use as semiconductors. Since there are the highest requirements with regard to their purity, special methods have been developed for their production.

It is known that compounds such as gallium arsenide can be produced in the required purity by dissolving at an elevated temperature and subsequent precipitation from the liquid phase with a lowering of temperature, with simultaneous epitaxial growth. A melt of a metal serves as a solvent. In order to eliminate contamination by foreign metals as far as possible, the metallic component of the binary system is preferably selected as a material for the metal melt, that is to say in the case of gallium arsenide for example gallium itself.

Methods of production and modes of operation hitherto known have a number of disadvantages, however.

For each individual attempt at growth, the gallium for the melt on the one hand and the corresponding quantities of doped or undoped gallium arsenide needed on the other hand have to be freshly weighed out. The quantity of gallium arsenide has to be precisely matched to the quantity of gallium because, before the beginning of the growth on the surface of the substrate, a defined layer of the surface of the substrate is removed by so-called thermal etching by means of the melt which undergoes superheating by 5° C beyond the saturation temperature in the course of this.

The weighing of small quantities of substance of maximum purity — the contamination of the gallium amounts to only 10^{-5} percent for example — makes such heavy demands on a clean mode of operation that it can only be realized with difficulty.

Further difficulties arise as a result of the fact that some of the gallium arsenide, which generally consists of a large number of small pieces, is lost during transfer to the gallium melt. In addition, with the large area of the gallium arsenide there is a risk of oxide layers forming or of foreign substances being absorbed which contaminate the melt.

On the other hand, the wetting of the small particles of gallium arsenide with the gallium melt is particularly poor. Accordingly, there are even undissolved particles in the melt in some cases. If — for example during a movement of the melt — these are brought on to the growing layer, the consequence is severe disturbance in the growth of the epitaxial layer. Further disturbances arise as a result of the fact that the gallium arsenide floats on the gallium because of its low density. At the high temperatures of the melt, which amount to up to 850° C during the saturation process, arsenic evaporates from the free surface and, as a result, alters the original composition of the melt.

The density of the melt rich in gallium arsenide resulting during the dissolving, like the density of the gallium arsenide, is lower than the density of the gallium. Since the pieces of gallium arsenide to be dissolved and the melt rich in gallium arsenide float on the gallium and so counteract mixing, the gallium arsenide is only dissolved very slowly in the gallium.

Finally, mention may be made of the difficulties which arise if a specific doping profile is to be produced simultaneously with the expitaxial growth, as a result of which a narrow temperature range must be adhered to. Then it is necessary to terminate the process at relatively high temperatures by complete removal of the melt from the substrate which was scarcely possible with the methods hithereto known.

SUMMARY OF THE INVENTION

It is the object of the invention to avoid or reduce the above-mentioned disadvantages.

According to one aspect of the invention, there is provided a method of liquid phase epitaxy comprising the steps of:

bringing a melt from which an epitaxial growth layer is to be precipitated into contact with an excess supply of a substance to be precipitated and simultaneously heating said melt until said melt is saturated,

separating said saturated melt from said supply of said substance to be precipitated and bringing said saturated melt into contact with a substrate in which said substance is to be precipitated,

cooling said melt continuously so as to deposit a growth layer of said substance epitaxially on said substrate, and

separating said saturated melt from said substrate.

According to a second aspect of the invention, there is provided an apparatus for liquid phase epitaxy comprising a refractory vessel rotatably through 180° and defining a pocket shaped recess for receiving a substrate, a storage receptacle for receiving a substance to form a melt and a substance for dissolution in the melt and wich is to be precipitated epitaxially on said substrate, a stopper for opening and closing said storage receptacle and means for displacing said storage receptacle inside the vessel for bringing said melt into contact with said substrate for epitaxial growth and for separating said melt from said substrate after termination of the growth process.

According to a third aspect of the invention, there is provided an apparatus for liquid phase epitaxy comprising a refractory crucible which is rotatable about its axis and which has a substantially G-shaped cross section, means for returning a substrate in said refractory crucible, a storage receptacle in a central region of said refractory crucible for receiving a substance to form a melt and a substance for dissolution in the melt and which is to be precipitated epitaxially on said substrate, and a stopper for opening and closing said receptacle, rotation of said crucible enabling movement of said melt into and out of contact with said substance for dissolution in said melt and into and out of contact with said substrate.

An advantageous further development of the device according to the invention for carrying out the method is characterised by a refractory crucible which is rotatable about its axis and the cross-section of which is substantially in the shape of a G having a storage compartment which is disposed in the central region and serves to receive the substance to be dissolved in the melt and which can be opened and closed by means of a closure,

the crucible being rotatable, after filling with thhe substance forming the melt, in such a manner that the melt can be brought into contact with the substance until it is saturated, be brought into contact with the substance for the epitaxial growth, and be removed from the substrate after termination of the growth process.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will now be described in greater detail, by way of example with reference to the accompanying drawings in which:

FIG. 1 is a diagrammatic sectional view of a first form of apparatus in accordance with the invention at the beginning of the method of the invention;

FIG. 2 is a view similar to FIG. 1 showing the apparatus at a second stage of the method;

FIG. 3 is a view similar to FIG. 1 showing the apparatus at a third stage of the method;

FIG. 4 is a view similar to FIG. 1 showing the apparatus at a fourth stage of the method;

FIG. 5 is a view similar to FIG. 1 showing the apparatus at the final stage of the method;

FIG. 6 is a diagrammatic sectional view of a second form of apparatus in accordance with the invention at the beginning of the method of the invention;

FIG. 7 is a view similar to FIG. 6 showing the apparatus at a second stage of the method;

FIG. 8 is a view similar to FIG. 6 showing the apparatus at a third stage of the method;

FIG. 9 is a view similar to FIG. 6 showing the apparatus at a fourth stage of the method; and

FIG. 10 is a view similar to FIG. 6 showing the apparatus at the final stage of the method.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The epitaxial growth of gallium arsenide from a gallium melt is selected as an example but it may be emphasised at the same time that the method according to the invention and the devices according to the invention are not restricted to these substances but are also suitable for other systems, for example Sn-GaAs, GaAlAs, In-InAs. With the Sn-GaAs system, the tin serves not only as a solvent but also as a doping material and highly doped compounds result.

A substrate wafer of gallium arsenide **1.1**, on the surface of which the epitaxial deposition is to be effected, is first wedged in a pocket-shaped recess in a vessel **1.2** which is substantially in the form of a boat and may appropriately consist of graphite. A storage compartment **1.3** which is adpated for displacement in the graphite boat **1.2** is now pushed outwards so for that gallium **1.5** can be introduced into its upper opening **1.4**.

Gallium arsenide **1.7** is introduced from the underside of the storage compartment **1.3** through a screw stopper **1.6**. It is a particular advantage of the device according to the invention that the quality of gallium arsenide **1.7** can be selected so great that it is sufficient not only for one attempt but for a whole series of attempts. The quality of gallium may appropriately be selected correspondingly great.

During the heating of the graphite boat **2.2** which now follows, as illustrated in FIG. **2**, the gallium-arsenide supply **2.7** remains in contact with the gallium melt **2.5**. The gallium arsenide is dissolved in gallium until saturation is reached. It is therefore merely necessary to maintain the system at a constant temperature for a sufficient length of time. In comparision with former arrangements it is an advantage in this case that the gallium arsenide, which has a lower specific gravity, is disposed at the lowest point of the melt. As a result, the saturation process is accelerated appreciably.

After the the gallium melt **2.5** has been saturated with gallium arsenide, the graphite boat **2.2** is turned through 180° about its longitudinal axis and now has the position which is illustrated in FIG. **3**. In this case, the saturated melt **3.5** is separated from the supply of gallium arsenide **3.7**. In the position, the melt **3.5** can be superheated by about 5° to 10° C by further heating of the system.

Then the melt **4.5** in the storage compartment **4.3** is drawn over the substrate **4.1** which is in the pocket of the vessel **4.2**, by means of the quartz rod **4.8**, as FIG. **4** shows. The elevated temperature is maintained in this position for the time being in order to remove some of the substrate surface by so-called thermal etching. Then the system is cooled down in accordance with a continuous temperature-time programme, gallium arsenide being precipitated epitaxially out of the melt **4.5** on to the substrate **4.1**.

If the growth is only to take place within a specific temperature range, as is necessary for example in order to achieve a specific doping profile, the melt **5.5** can easily be separated from the substrate **5.1** by turning through 180° into a position as shown in FIG. **5**, and in this manner the required doping profile can be obtained.

After the system has cooled down, the storage compartment **5.3** is pushed away from the substrate **5.1** again. The substrate **5.1** with the grown layers can then be removed from the pocket in the vessel **5.2**. Saturation of the gallium with the gallium arsenide agains takes place during a fresh heating period and then the individual method steps described are repeated so long as there is still a supply of gallium arsenide.

In a further embodiment of the device according to the invention, the filling with the components, the saturation of the gallium with the gallium arsenide, the homogenisation and the superheating of the melt, the actual growth of the process and finally the separation of the galloum melt from the substrate in order to terminate the growth process are not achieved by lateral displacement of the melt but by rotation in a crucible, the walls of which are so shaped that the individual method steps follow one another.

FIGS. **6** to **10** show — again illustrated partially diagrammatically — one possible form of construction.

A crucible of graphite **6.2**, the cross-section of which is substantially in the form of a G, contains in the centre region, a storage compartment **6.3** to receive the gallium arsenide **6.7**. It is first brought into such a position that its mouth **6.4** faces upwards and the gallium **6.5** is then introduced through this. Then it is turned in counter-clockwise direction through 270° into a position illustrated in FIG. **7**, whereupon the gallium **7.5** and the gallium arsenide **7.7** are now in contact with one another. As in the first example, the gallium **7.5** is above the gallium arsenide **7.7** so that here, too, after the heating to the melting temperature, a rapid mixing of the molten components can take place until there is saturation.

As a result of turning back through 180° into a position which is shown in FIG. **8**, the saturated solution **8.5** is separated from the supply of gallium arsenide **8.7** and

is brought on to the substrate **9.1** by further turning back through 180° as shown in FIG. **9.** The substrate **9.1** may appropriately be gripped by means of a quartz pin or a graphite dog present in the crucible cover. During the transition from the position shown in FIG. **8** into the position shown in FIG. **9,** impurities present on the melt **8.5,** for example oxide skins or dust, are stripped off as the melt **8.5** brushes past the wedge-shaped edge **8.8.**

After termination of the growth process, the crucible is turned through 180° in a counter-clockwise direction. It is then in a position as illustrated in FIG. **10.** In this case, the melt **10.5** is separated from he substrate **10.1** which can be removed, with the grown layer, after cooling down. After the crucible has been turned into the position illustrated in FIG. **7,** the individual method steps can be repeated with the crucible as with the graphite boat so long as there is a supply of gallium arsenide present.

The crucible construction has the advantage over the graphite boat first described that no graphite parts are slid one over the other. As a result, a disturbing abrasion of graphite is avoided.

It will be understood that the above description of the present invention is susceptible to various modifications changes and adaptations.

What is claimed is:

1. An apparatus for liquid phase epitaxy, comprising a horizontally disposed refractory vessel rotatable through 180° and defining a pocket shaped recess for receiving a substrate, a storage receptacle for receiving a substance to form a melt and a substance for dissolution in the melt and which is to be precipitated epitaxially on said substrate, said vessel including a stopper for opening and closing said storage receptacle, and means for displacing said storage receptacle longitudinally inside the vessel for bringing said melt into contact with said substrate for epitaxial growth and for separating said melt from said substrate after termination of the growth process.

2. An apparatus as defined in claim **1,** wherein said refractory vessel consists of graphite.

3. An apparatus as defined in claim **2,** wherein said displacing means comprises a quartz rod.

4. An apparatus as defined in claim **1,** wherein said storage receptacle is of a size sufficient to hold the necessary quantity of said substances for a plurality of epitaxial growth.

5. Apparatus for use in liquid phase epitaxy, comprising: a horizontally disposed refractory vessel having an extended upper wall; a substrate retained at an inner section of said upper wall; a storage receptacle for receiving a substance to form a melt and a substance to be precipitated on said substrate; means to move said receptacle longitudinally within said vessel from a position external of said upper wall, whereby to change said receptacle, to a position underlying a portion of said wall, whereby to seal said receptacle; the entire structure of said vessel and sealed receptacle being adapted to be inverted; and said means to move being adapted to further move the inverted receptacle along said wall to a position overlying said sustrate whereby to expose the substrate to the melt contained in the receptacle.

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