

[54] **GROWTH APPARATUS FOR A LIQUID GROWTH MULTI-LAYER FILM**

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[51] Int. Cl. **B05c 3/00**

[58] Field of Search..... 118/415, 422, 429; 117/201; 148/171, 172, 173

[56] **References Cited**

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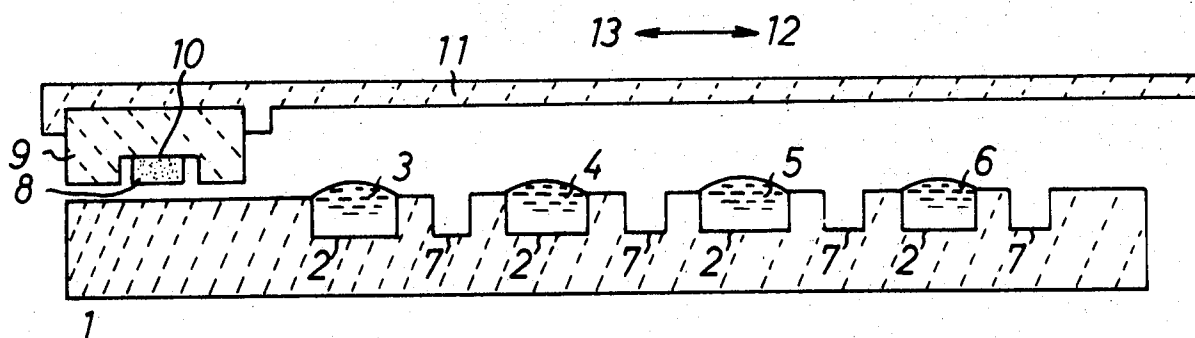
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[57] **ABSTRACT**

A growth apparatus for a liquid growth multi-layer film, in which a growth substrate is housed in a hollow of a first supporter, in which a plurality of molten liquids are respectively provided in a plurality of hollows arranged in regular spaces on one surface of a second supporter, and in which one of the first supporter and the second supporter is moved with respect to the other in opposing the growth substrate with the molten liquids. In accordance with the present invention, the growth substrate provided in the first supporter is shifted closely to and at the upper side of the molten liquids, and the second supporter is provided with a plurality of small hollows each at a space between adjacent hollows of the second supporter.

3 Claims, 4 Drawing Figures



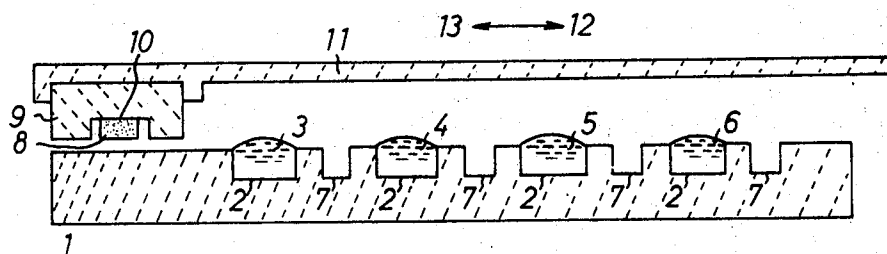


Fig. 1

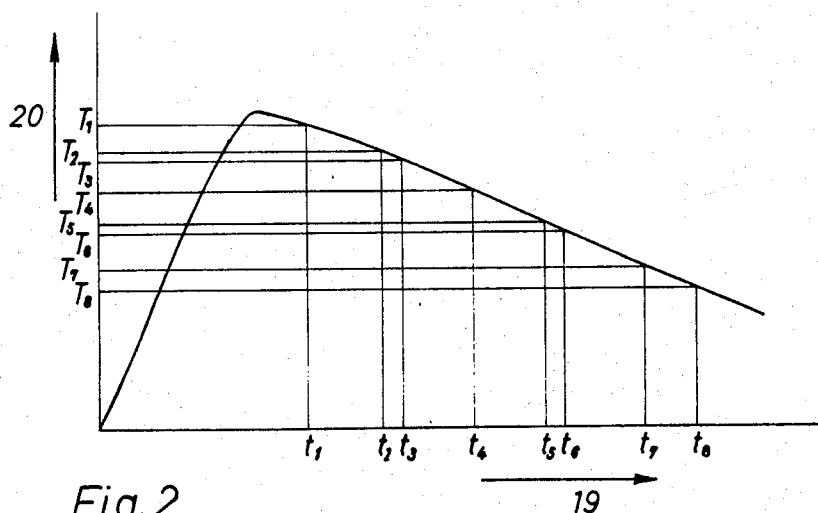


Fig. 2

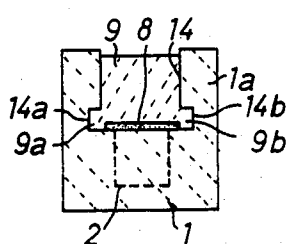


Fig. 3

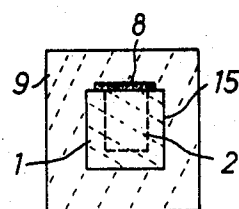


Fig. 4

GROWTH APPARATUS FOR A LIQUID GROWTH MULTI-LAYER FILM

This invention relates to a liquid growth apparatus for a semiconductor and the like and, more particularly, to an apparatus of growing a multi-layer film on a crystal substrate through the use of a liquid growth method.

In conventional growth apparatus for a multi-layer film, molten liquids are inevitably mixed with one another as a result of the movement of the molten liquids on the substrate, and no means is provided for removing the molten liquids stuck on the substrate. Accordingly, control of the impurity concentration is difficult or, in the case of simultaneously growing some different materials, grown layers of desired materials cannot be obtained.

An object of this invention is to provide a growth apparatus for a multi-layer film capable of producing a multi-layer film of low impurity concentration.

Another object of this invention is to provide a growth apparatus for a multi-layer film capable of readily producing a multi-layer film having more layers than three.

Another object of this invention is to provide a growth apparatus for a multi-layer film capable of independently controlling temperatures for growing respective layers.

Another object of this invention is to provide a growth apparatus for a multi-layer film capable of readily producing a grown film of different material layers.

A further object of this invention is to provide a growth apparatus for a multi-layer film capable of producing a device having a multi-layer construction formed by the same or different materials, such as a double hetero junction, a transistor, a Gunn diode, a transit-time negative resistance diode and so on.

In accordance with the principle of this invention, a substrate for growth is disposed on molten liquids, and the molten liquids are so arranged as not to get mixed with one another. Moreover, the substrate or the liquids are moved with respect to each other.

In the apparatus of this invention, a semiconductor substrate used as a seed crystal is moved on molten liquids which are prepared at some different locations for growing. This invention may include means at a movement path of the substrate between adjacent molten liquids for avoiding mutual mixing of the molten liquids and for removing the molten liquids stuck on the substrate. Moreover, if necessary, the substrate may be stopped without contact to any molten liquids at the movement of the substrate.

The principle of this invention will be clearly understood from the following detailed discussion taken in conjunction with the accompanying drawings, in which:

FIG. 1 is a longitudinal section illustrating an embodiment of this invention;

FIG. 2 is a characteristic curve explanatory of the temperature process in an apparatus of this invention;

FIG. 3 is a transverse section of another embodiment of this invention; and

FIG. 4 is a transverse section of another embodiment of this invention.

A preferred example of this invention will be described with reference to FIG. 1. A jig or boat 1 for

growing films has a plurality of hollows 2 therein which are filled with molten liquids 3, 4, 5 and 6 respectively. The portions of the jig between adjacent liquid-filled hollows 2 are formed with additional preferably smaller hollows, 7, respectively. A semiconductor substrate 8 used as a seed crystal is housed in a hollow 10 made in a slider 9. The slider 9 is pulled in the righthand direction 12 by the use of a bar 11 controlled by gravity or a suitable mechanical or motor driver, not shown, so that the semiconductor substrate 8 is shifted onto the molten liquid 3. The slag and excess of the molten liquid 3 are removed by the slider 9 as the latter moves over and in contact with the upper surface of the jig, and the substrate 8 is placed opposite the first hollow 2 in contact the molten liquid 3 so that film growth on the substrate is started. Upon completion of the film growth by the molten liquid 3, the substrate 8 is then moved opposite the second hollow 2 in contact with the molten liquid 4 for growth of the second film. The same operations are repeated for the subsequent layers to achieve multi-layer growth. The slag and excess of the molten liquid 3 are scraped into adjacent hollow 7 formed in the jig 1 between the hollows containing molten liquids 3 and 4 so that molten liquid 3 is not mixed with any of the molten liquid 4. In this manner, none of the molten liquids 3, 4, 5 and 6 is mixed with the other. Moreover, any of the molten liquid stuck on the substrate can be removed at the corner edge of the next adjacent hollow 7.

FIG. 2 shows an example of the temperature process in the multi-layer liquid growth apparatus of this invention. The abscissa 19 and the ordinate 20 represent time and liquid temperature respectively.

A further concrete description of the operations of this invention will be given below in connection with FIGS. 1 and 2. At the time t_1 assuming a temperature T_1 , the substrate 8 is pulled onto the molten liquid 3, and growth is achieved until the time t_2 assuming a temperature T_2 , when the substrate 8 is pulled away from the molten liquid 3. At the time t_3 assuming a temperature T_3 , the substrate 8 is pulled onto the molten liquid 4 to carry out growth thereof until the time t_4 assuming a temperature T_4 , and then the substrate 8 is pulled away from the molten liquid 4. The same operations are effected at times t_5 , t_6 , t_7 and t_8 to provide a multi-layer liquid growth film having four liquid-grown layers.

Other examples of this invention will be described in connection with FIGS. 3 and 4 illustrating transverse sections of the apparatus of this invention. If the slider 9 is so light as to be floated on the liquids 3, 4, 5 and 6, the molten liquids enter between the boat 1 and the slider 9. To avoid this defect, the slider 9 is adapted not to float during its movement. In an example shown in FIG. 3, the upper part 1a of the boat 1 is so extended as to have a straight groove 14 along the longitudinal direction of the boat 1. The groove 14 has two small grooves 14a and 14b at opposite longitudinal walls thereof. The slider 9 has two longitudinal projections 9a and 9b, so that the slider 9 is slidable along the groove 14 in coupling the projections 9a and 9b with the small longitudinal grooves 14a and 14b respectively. Other reference numerals 2 and 8 are the same parts as shown in FIG. 1.

In an example shown in FIG. 4, the slider 9 carrying the substrate 8 has a center opening 15 along the longitudinal direction thereof, so that the boat 1 having the

hollows 2 for the molten liquids is movable in the longitudinal opening 15 of the slider 9.

Small hollows 7 such as shown in FIG. 1 are also provided between adjacent hollows 2 in the both examples shown in FIGS. 3 and 4.

As to the temperature process, it is not always necessary to effect unidirectional cooling of the grown layer with the lapse of time in the foregoing examples. For example, it is also possible to elevate and then lower the temperature in an entire growth process for multi-layers. Moreover, growth of each layer may be based on a temperature difference method, such that a temperature difference is caused between the substrate 8 and the molten liquid 3, 4, 5 or 6 by radiation or heating with the use of a bar 11 or the like.

In FIGS. 1, 3 and 4 the slider 9 carrying the substrate 8 may be fixed while the boat 1 carrying the molten liquids 3, 4, 5 and 6 may be moved.

Any substances may be used as the molten liquids in this invention so long as they are capable of liquid growth. The jig 1 for growing may be formed by any material which does not react with the raw materials for growing and the substrate, and which permit the growth of layers of low impurity concentration, such as graphite, glassy carbon, quartz, ceramic or the like.

In our experiments, a multi-layer liquid grown film having four layers was obtained by alternately growing $\text{Al}_x\text{Ga}_{1-x}\text{As}$ and GaAs on a GaAs substrate. The substrate used was the plane (100) of N-type GaAs added with Te having a carrier concentration of $10^{18}/\text{cc}$. The molten liquid 3 was a mixture of Ga of 2 grams, Al of 6 milli-grams, GaAs of 0.2 grams and Sn of 20 milli-grams; the molten liquid 4 a mixture of Ga of 2 grams and GaAs of 0.3 grams; the molten liquid 5 a mixture of Al of 6 milligrams, GaAs of 0.2 grams and Zn of 10 milli-grams; and the molten liquid 6 a mixture of Ga of 2 grams, GaAs of 0.3 grams and Zn of 10 milli-grams. The purity of Ga, GaAs and Zn was 99.9999 percent, while purities of Sn and Al were 99.999 percent and 99.99 percent respectively. The jig was formed by graphite and baked at a temperature of 1000°C at a low atmospheric pressure of about 10^{-6} mm Hg for two hours. The growth was achieved in an atmosphere of hydrogen. The stream of hydrogen was passed in the direction indicated by an arrow 12. The temperature process was controlled at a cooling rate of 1°C to 3°C per minute. The growth using the molten liquid 3 was carried out from 850°C to 840°C , the growth using the molten liquid 4 from 839°C to 838°C or 836°C , the growth using the molten liquid 5 from 837°C to 835°C or about 820°C , and the growth using the molten liquid 6 from about 820°C to 800°C . A grown layer of N-type $\text{Al}_x\text{Ga}_{1-x}\text{As}$, a grown layer of GaAs of low impurity concentration, a grown layer of P-type $\text{Al}_y\text{Ga}_{1-y}\text{As}$ and a grown layer of P-type GaAs which were obtained in the above experiments, have thickness of 3 microns to 5 microns, 1 microns to 12 microns, 3 microns to 5 microns, and 4 microns to 7 microns respectively. The impurity concentration of the GaAs grown layer of low impurity concentration was as low as $10^{16}/\text{cc}$, while that of the P-type GaAs grown layer of high impurity concentration was as high as $10^{18}/\text{cc}$. Thus, the impurity concentration can be controlled over as wide range as containing three figures. A grown layer of lower impurity concentration can be obtained by using as the addi-

tive impurity a material of low vapor pressure and of small diffusion coefficient. Moreover, no intermixture of the molten liquids for the growth of the GaAs layer and the AlGaAs layer could also be ascertained by the X-ray analysis of the grown layers and by the spectroscopic analysis thereof using laser emission spectrum. The values of x and y in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ and $\text{Al}_y\text{Ga}_{1-y}\text{As}$ were a range 0.2 to 0.5 and a range 0.2 to 0.4 respectively. This enables the formation of multi-layer liquid grown layers made by several kinds of materials.

A double hetero junction laser produced by the above process using the apparatus of this invention was an excellent laser of low temperature dependency, such that its threshold current density was as low as $4 \times 10^3 \text{ A/centi-meter}^2$ and $2 \times 10^4 \text{ A/centi-meter}^2$ at 77°K and 300°K respectively. The laser emission wave length was $8300\text{\AA}$ at 77°K and 300°K respectively, and these are equal to those of light from the GaAs region of lower impurity concentration.

Accordingly, the apparatus of this invention can also be employed for producing devices of a multi-layer construction formed by the same or different materials, such as a transistor, a Gunn diode, a transit-time negative resistance diode and the like in addition to the double hetero junction laser.

What we claim is:

1. A growth apparatus for a liquid growth multi-layer film, comprising:

a first supporter having a downwardly facing hollow housing a growth substrate, the substrate face on which the film is to be grown lying substantially in the face plane of said supporter, and said face plane terminating in sharply defined edges;

a second supporter having in the upwardly facing surface thereof a plurality of longitudinally spaced and aligned, second hollows, the first and alternate hollows therefrom containing separate ones of a plurality of molten liquids from which said multi-layer film is to be grown and the remaining hollows being void;

said first supporter overlying, and in longitudinal alignment with, said second supporter and said face plane closely adjacent said surface;

said supporters being configured to include guide structure whereby to maintain and fix the described spatial relationship of the supporters when assembled; and

means for longitudinally moving said supporters relative one another whereby one of said defined edges sequentially skims off the exposed face of each of said molten liquids, each removed liquid being received in the next adjacent void hollow, and the substrate sequentially contacting each skimmed molten liquid to effect said growth.

2. A growth apparatus according to claim 1, whereby said configuration the first supporter is slidably coupled with a straight groove provided at the upper side of the second supporter, and the first supporter has a pair of straight projections which are coupled with a pair of small grooves in the straight groove.

3. A growth apparatus according to claim 1, whereby said configuration the first supporter is in the form of a vertically oriented annulus and the second supporter is slidable therethrough.

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