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(54) METHODS OF GROWING MULTILAYER SEMICONDUCTOR CRYSTALS

(71) We, WESTERN ELECTRIC COMPANY, INCORPORATED, of 195 Broadway, New York City, New York State, United States of America, a Corporation organized and existing under the laws of the State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a solution epitaxy method for the growth of multilayered semiconductor crystal structures of Group III—V compounds of the Periodic Table of the Elements. An example of the use of the method is for the growth of a multilayered Group III—V structure, termed a double heterostructure (DH), which is of particular interest for use as a junction laser.

Recently, interest in junction lasers operating over a temperature range of from 250° to 300°K (room temperature) has been stimulated by reported success in lowering the threshold current density (J_{th}) for lasing from prior art levels of the order of 25,000 amperes per square centimeter or greater to as low as 6,000 amperes per square centimeter. Such lower thresholds facilitate room temperature operation by reducing overheating of the device.

As discussed in a communication in *Journal of Applied Physics, 41,* 150 (1970) by I. Hayashi and M. B. Panish, the aforementioned lower threshold densities were attained in a multilayered structure, termed a single heterostructure (SH), comprising contiguous regions of a wide band gap material (e.g., p-$Ga_{1-x}Al_xAs$) and a narrow band gap material (e.g. GaAs) separated by a heterojunction. A heterojunction is defined as the interface between narrow, and wide band gap regions and is further designated n-n, p-p, n-p or p-n depending on the majority carrier type on either side of the junction. In the SH diode a p-n junction was located in the narrow band gap region thereby defining an intermediate region, between the p-n junction and heterojunction, in which radiative recombination of holes and electrons occurs when the diode was forward biased. It is believed that confinement of electrons as well as photons in the intermediate region combine to produce lower thresholds. It has been recognized further that these advantageous results require that the thickness of intermediate region be less than the diffusion length of injected carriers and in any event preferably less than about 2.0 μm in the SH. Accordingly, attention has focused upon the development of a technique suitable for the growth of such structures with particular attention being given to controlling the thickness of the intermediate region. One such technique, for fabricating SH laser diodes, a solution epitaxy procedure carried out in a tipping apparatus, is the subject matter of British Patent Application No. 62286/69 (Serial No. 1293408).

Briefly, the procedure for fabricating an SH diode involves growth by solution epitaxy in a tipping apparatus including a movable substrate holder adapted with means for removing deleterious oxide contaminants from the surface of a source solution prior to growth. In the operation of the process, a gallium - arsenide wafer is deposited upon a source solution cleaned as noted, and epitaxial growth effected thereon. During the course of the process, an epitaxial film containing a p - type dopant is grown upon the substrate and during growth and subsequent thereto, diffusion of the p - type dopant into the n - type substrate is effected, so resulting in the formation of a p-n junction in the substrate.

According to the invention a method of growing a multilayer semiconductor crystal structure in a crystal growth apparatus hav-

ing a seed holder and a plurality of containers for source solutions comprises the steps of inserting a seed of a group III—V compound semiconductor, applying the seed to a first container in which is a source solution comprising a first group III element, a second group III element and the compound dissolved therein, controlling the temperature so as to grow a first epitaxial layer thereon, providing relative movement between the holder and the containers so as to apply the seed and first layer to a second container in which is a source solution comprising the said first element and said compound dissolved therein with or without said second element, which, if present, is in a smaller percentage than in the first solution, and regulating the temperature so as to grow a second epitaxial layer having a thickness of 1.5 μ or less on the first layer, the composition of the solutions being such that the first layer is a wide band-gap layer and the second layer is a narrow band-gap layer and further providing relative movement between the holder and a third container, in which is a source solution comprising the first element, the second element in a greater percentage than in the second solution and the compound dissolved therein and further regulating the temperature so as to grow a third layer, the third layer forming a wide band-gap layer from the third solution over the narrow band-gap layer.

Illustratively a tipping apparatus or a sliding apparatus may be utilized to bring the solutions and seed into contact with one another. In either case, however, it has been found that the establishment of a temperature gradient, in which the top of the solutions are at lower temperature than the bottom thereof, is desirable for the growth of a thin narrow band-gap layer less than 1.5 μm in thickness.

These multilayered structures with appropriate doping are particularly useful as junction lasers and permit for a given temperature operation at lower thresholds than heretofore possible. In addition, however, these same structures with or without doping can also function as optical waveguides in which light propagates in a narrow band-gap layer and is guided by the different index of refraction of contiguous wide band-gap layers.

In one embodiment for the growth of a double heterostructure laser diode, a first solution of Ga-Al-GaAs saturated with As and containing an n - type dopant is brought into contact with an n - type GaAs seed to effect growth thereon of a wide band gap, n-$Ga_{1-x}Al_xAs$ epitaxial layer. Then, a second solution of Ga-GaAs saturated with As and containing preferably substantially compensating dopants is brought in contact with the seed to effect growth of a p - type, substantially compensated, narrow band-gap intermediate layer. Finally, a third solution of Ga-Al-GaAs saturated with As and containing a p - type dopant is brought into contact with the seed to effect growth of a wide band gap, p-$Ga_{1-x}Al_xAs$ layer, thereby completing the double heterostructure.

The invention can be better understood from the following more detailed description of embodiments thereof in which:

FIG. 1A is a front elevational view, partly in cross-section, of a typical tipping apparatus which may be employed in the practice of the invention;

FIG. 1B is a top view of the boat and slider shown in the apparatus of FIG. 1A;

FIG. 2A to 2E are cross-sectional views in successive stages of manufacture of a double heterostructure junction laser fabricated in accordance with a preferred embodiment of the present invention;

FIG. 3A is a front elevational view, partly in cross-section, of a typical sliding apparatus which may be employed in the practice of the invention; and

FIG. 3B is a front elevational view of an alternative slider arrangement for use in apparatus of FIG. 3A.

With reference now to FIGS. 1A and 1B, there is shown a typical crystal growth apparatus which may be utilized in the practice of the present invention comprising a crystal growth tube 11, typically comprised of fused silica, having an inlet 12 and an outlet 13 for the introduction and removal of gases, respectively, and a boat assembly 14. Boat 14 includes a pair of stops 25 and 26 and a recess for rigidly carrying a seed or substrate 19. Disposed in the boat is a movable solution holder 15 having wells 16*a*—16*c* for containing source solutions. Holder 15 is also adapted to pass over groove means 18 in boat assembly 14 for removing oxides and associated solid contaminants from the bottom surface of each of the source solution contained in wells 16*a*—16*c*. The apparatus also contains a thermocouple well 20 and thermocouple 21 for determining the temperature of the system. Tube 11 is shown inserted in furnace 22 adapted with a viewing port 23, furnace 22 being positioned upon cradle 24 which permits tipping of the growth tube.

Referring now to an exemplary technique for growing a double heterostructure laser diode, a suitable n - type gallium arsenide substrate materials obtained, typically from commercial sources. For the intended purpose, the seed or substrate member selected should evidence a carrier concentration within the range of about 10^{17}—10^{19} electrons per cubic centimeter. Selection of a material containing less than about 10^{17} electrons per cubic centimeter would probably exhibit insufficient conductivity for c.w. laser operation without overheating. The maximum

carrier concentration is dictated by practical considerations. The material so obtained is next lapped and cleaned in accordance with conventional techniques to yield suitable surfaces. A cross-sectional view of a typical substrate member is shown at 31 in FIG. 2A.

Next, source solutions I, II and III typically consisting of gallium, aluminium, gallium arsenide, and appropriate dopants are prepared. This end is attained by adding known (excess) quantities of solid gallium arsenide (99.9999% purity), obtained from commercial sources, to known quantities of gallium (99.9999% purity) and heating the resultant mixture in a pure hydrogen atmosphere to a temperature sufficient to completely dissolve the gallium arsenide. The solution is then cooled and the requisite amount of aluminium and dopant are added so as to result in solutions of the desired composition upon subsequent heating. The amounts of gallium, gallium arsenide, and aluminium are dictated by considerations related to the gallium - aluminium - arsenic ternary phase diagram as well as the desired band gaps, whereas the quantity of dopant employed is dictated by the doping level (and consequent resistivities) desired in the several regions of the resultant structure.

Each solution contains an excess of GaAs. An example of solutions that may be used is as follows: (1) solution I comprises Ga, Al and GaAs with 1.5—2.5 mg Al/gm Ga and an n - type dopant (e.g., 10—20 mg Sn/gm Ga, 1—3 mg Si/gm Ga or 0.1—1 mg Te/gm Ga); (2) solution II comprises Ga and GaAs or Ga, Al and GaAs with compensated doping (e.g., 1—4 mg Si/gm Ga or about 1 mg Si and 1—2 mg Zn per gram of Ga) and provided that in the latter case, solution II contains a smaller percentage of Al than either solutions I or III; and (3) solution III comprises Ga, Al and GaAs with 2—3 mg Al/gm Ga and a p - type dopant (e.g., 3—5 mg Zn/gm Ga). These materials and concentrations are of course merely illustrative.

The components of solutions I, II and III are next placed in wells 16*a*, 16*b* and 16*c*, respectively, of holder 15 which is initially disposed against wall 14*a* of boat 14, the components being mixed and dissolved during subsequent heating. Then, the substrate member or seed 19 is inserted in the recess in the base of boat 14 and the system flushed with nitrogen. After flushing the system, prepurified hydrogen is admitted thereto and the temperature elevated to within the range of 700—1100°C depending upon the composition of the solution selected. After attaining the maximum temperature (e.g., 870°C), the system is cooled at a predetermined rate (e.g., 1—6°C/min) and upon reaching the desired first tipping temperature (e.g., 850°C), the apparatus is activated by tipping the boat in the direction of arrow 1, thereby causing the leading edge 15*a* of the solution holder 15 to abut against end wall 14*d* of boat 14 and causing solution I to be deposited on seed 19. Concurrent with the sliding motion of holder 15, grooves 18 remove the oxide scum from the bottom surface of the solution I. The controlled cooling program is continued. An n-$Ga_{1-x}Al_xAs$ film 32 so grown on the n - type GaAs seed 31 may be seen by reference to FIG. 2B.

Upon further cooling, the system reaches a second tipping temperature (e.g., 830°C) whereupon the boat is tipped in the opposite direction as indicated by arrow 2, thereby causing the edge 15*b* of holder 15 to abut against stop 26 and concurrently causing grooves 18 to remove the oxide scum from the bottom surface of solution II which is now deposited on seed 19. Growth for a prescribed time dependent upon the desired film thickness and cooling rate is continued to form a narrow band gap, intermediate p-GaAs layer 33 as shown in FIG. 2C. A p-n heterojunction 32*a* is thereby formed at the interface between layers 32 and 33.

Finally, upon further cooling, a third tipping temperature is reached and the tube 11 is rotated about its longitudinal axis until holder 15 abuts against side wall 14*d* of boat 14. Then, the boat is tipped in the direction of arrow 3 until holder wall 15*b* and boat wall 14*c* abut, thereby again causing grooves 8 to remove the oxide scum on the bottom of solution III which is now disposed over the seed 19. Growth is continued for time period sufficient to form a wide band gap, p-$Ga_yAl_{1-y}As$ region 34 as shown in FIG. 2D.

The viewing port 23, utilized to visually observe each tipping step, advantageously produces a temperature gradient in a direction substantially normal to the growth surface as a result of heat flow out of the port window. This gradient, with the solution hotter at its bottom near the seed than at its top, causes the solution to precipitate to a greater degree at the top (i.e., on the floating nuclei), thereby permitting the growth of very thin intermediate layers as preferred for low threshold lasing. Layers less than 1 μm thick have been fabricated.

Inasmuch, as the apparatus shown in FIG. 1A does not include means for controlling the magnitude of this temperature gradient or means to permit growth of more than three layers, the apparatus of FIG. 3A may be used in which the view port is eliminated and an auxiliary heater is provided to produce a controllable temperature gradient. The apparatus comprises a growth tube 111 having an inlet 112 and an outlet 113 for the introduction and removal of gases, respectively, and a solution holder 115, typically

cylindrical in cross-section, and having a plurality of wells 116*a*—116*d* for containing source solutions. Slidably inserted in a channel in solution holder 115 is substrate holder 114 having a recess for carrying a seed 119. The holder 114 abuts against stop 117 to prevent translational movement to the left. It will be noted here that the grooves 18 of the apparatus of FIG. 1A have been omitted inasmuch as substrate holder 114 is typically made of graphite with a relatively rough upper surface 114*a* sufficient to remove oxide scum from the bottoms of solutions 116*a*—116*d*. The tube 111 also contains a port 120 to permit the insertion of a slender tube 121 into the thermocouple well 122 in the base of solution holder 115. Within the tube 121 is inserted a thermocouple 123 for measuring the temperature of the substrate. Inserted from port 124 is a rod 125, or other mechanical means, for sliding solution holder 115 with respect to substrate holder 114. Tube 111 is shown secure in a furnace 126 (having main heating elements 127 and 128) by means of packing members 129 and 130. Auxiliary heater 131, which produces the aforementioned temperature gradient, is disposed between the bottom of solution holder 115 and the interior of the furnace wall. Note that the viewing port 23 of the apparatus of FIG. 1A has accordingly been omitted. In the sliding apparatus of FIG. 3A, the compositions of solutions I, II and III and the programmed procedure described with respect the tipping apparatus of FIG. 1A may also be utilized in the apparatus of FIG. 3A. In this case, however, the temperature gradient advantageous to the growth of thin intermediate layers is provided by auxiliary heater 131. At each appropriate temperature, corresponding to the tipping temperatures of the previous method, rod 125 is pushed so as to slide holder 115 and thereby dispose solutions I, II and III sequentially over seed 119. Of course, one skilled in the art would readily appreciate that the solution holder could be fixed and the substrate holder be moved relative thereto.

As shown in FIG. 3A, however, holder 115 is provided with a fourth well 116*d* illustratively for carrying a solution IV containing Ga, an excess of GaAs and a p - type dopant (e.g., 10 mg Zn/gm Ga or 2—3 mg Ge/gm Ga). This solution produces a p-GaAs layer 35, as shown in FIG. 2E, on which may be subsequently formed an ohmic contact 37 by means well known in the art, thereby alleviating the difficulty of making such contacts on the mixed crystal layer 34. Ohmic contact 36 on GaAs substrate 31 may also be formed by techniques well known in the art.

The space or gap between upper surface 114*a* of seed holder 114 and the surface 115*a* of solution holder 115 is typically about 5—10 mils, except that this gap adjacent surface 115*b* is only about 1—2 mils. It was found that the narrower space at 115*b* effectively wiped the last solution from the seed surface so that no substantial growth occurred after the seed was removed from solution IV and moved into region 115*b*. Finally, the holders may be removed from the tube by opening tapered joint 140.

The flared shapes of the bottom of the solution wells 16*a*—16*d* and the aforementioned spacing permit the maintenance of a continuous solution layer over the seed once the first solution has been applied. Although this feature is not absolutely necessary, it has been found that more consistently good quality structures are obtained when such a spacing and well shape are used.

Several techniques, taken separately or in combination, may be utilized to increase the area of the growth surface, thereby enabling the fabrication of a device with greater usable cross-sectional area. For example, as shown in FIG. 3B, the seed 119 is placed in a well 132 in holder 114, with the well being sufficiently deep that the top surface of the seed lies below the top surface 114*a* of the seed holder. Consequently, after each solution is removed from the seed, a small portion of that solution remains thereon, with the result that the next solution placed on the seed adheres to substantially the same surface area as the prior solution. In addition, the entire apparatus, or at least the solutions, may be subjected to vibratory motion during at least a portion of the time that each solution is in contact with the substrate, thereby increasing the area of contact between the solution and seed. Finally, on the substrate, prior to the solution I-step, may be grown a fresh n-GaAs layer.

The same procedures may be utilized to fabricate multilayered structures of other III—V semiconductor compounds and mixed crystals thereof. However, it is believed that better structures result if the lattice parameters of the pure binary compounds (e.g., GaAs-AlAs or GaP-AlP) are substantially the same. In any event, the structures, as previously mentioned are of special interest for use as optical waveguides.

Example

This example describes the fabrication in accordance with the invention of a low threshold junction laser utilizing the sliding apparatus shown in FIG. 3A.

A silicon doped gallium arsenide wafer (about 0.25 inch × 0.5 inch × 20 mils) with about 4×10^{18} electrons per cubic centimeter having faces perpendicular to the <100> direction, obtained from commercial sources, was selected as a substrate member. The wafer was lapped with 305 carborundum,

rinsed with deionized water, and etch-polished with a bromine - methanol solution to remove surface damage.

Four solutions were then prepared in the following manner. First, the following quantities of materials were weighed out. For solution I, 1 gm Ga, 100 mg, GaAs (undoped), 2 mg Al and 15 mg Sn. For solution II, 1 gm Ga, 100 mg GaAs (undoped) and 1 mg Si. For solution III, 1 gm Ga, 50 mg GaAs (undoped), 3 mg Al and 5 mg Zn. For solution IV, 1 gm Ga, 75 mg GaAs (undoped) and 32 mg Ge. For each solution the Ga plus GaAs was briefly preheated to 900°C under H_2 in a graphite solution holder. The seed and the four prepared solutions of Ga plus GaAs were placed in their respective wells in the apparatus of FIG. 3A. The remainder of the solid components which had been weighed out were then placed into the proper wells with the premixed Ga plus GaAs and were mechanically forced under the surface of the liquid Ga to ensure good contact upon subsequent heating. The holder assembly was then placed into a fused silica tube as illustrated in FIG. 3A. Hydrogen was passed through the tube to flush out air. After flushing for about 10 minutes the tube containing the holders was placed into the furnace which was at 870°C. The auxiliary heater, which consisted of a single loop of about 2 feet of 20 mil nichrome wire heated by 20 volts a.c., was on during this operation. The temperature as measured by the thermocouple was allowed to rise to about 870°C and then a cooling rate of 3°C/minute was established. At 850°C the solution holder was moved so that solution I came into contact with the seed. A mechanical vibrator was used to agitate the solution slightly while cooling to 830°C occurred. At 830°C the solution holder was moved so that solution II covered the seed and remained there with vibration for about 15 seconds. The solution holder was then again moved so that the seed was disposed under the solution III, where it was held for 30 seconds (with vibration). The solution holder was then again moved so that the seed was placed under solution IV and kept there for 60 seconds (with vibration), following which the seed holder 114 was moved again so that the close fitting upper graphite surface 115*b* of solution holder 115 wiped the residual of solution IV from the seed. During this entire procedure the cooling rate of 3°C/minute was maintained. Following the last step the tube was removed from the furnace and allowed to cool to room temperature. This procedure resulted in a wafer 31 of n - type GaAs upon which were deposited, epitaxially, four layers as shown in FIG. 2E. The first layer 32 on the substrate 31 is estimated to consist of n-$Ga_{1-x}Al_xAs$ with x approximately 0.3—0.5, doped by Sn to about 10^{18} electrons/cm^3. An n-n heterojunction 31*a* was formed at the interface between layers 31 and 32. The second layer 33 was GaAs doped by Si (and possibly Zn from diffusion from the following layer) compensated, but p - type. A p-n heterojunction 32*a* was formed at the interface between layers 32 and 33. The third layer 34 was estimated to be p-$Ga_{1-x}Al_xAs$ with x approximately in the range 0.3—0.5 doped p - type by Zn in the range of 10^{18}—10^{19} holes/cm^3. A p-p heterjunction 33a was located at the interface between layers 33 and 34. The fourth layer 35 was GaAs doped p - type by Ge to about 10^{18} holes/cm^3. This resulted in another p-p heterojunction 34*a* between layers 34 and 35.

The thicknesses of the layers 32—35 in a section measured were approximately 5 μm, 1.5 μm and 2—15 μm, respectively. The separation of the p-n heterojunction 32*a* from the p-p heterojunction 33*a* was therefore approximately 1.5 μm.

A non-heat sinked laser diode was then prepared from the wafer so obtained for the purpose of evaluating the threshold current density. This end was achieved by initially skin diffusing Zn at high concentration (10^{20} Zn/cm^3) to a depth of 0.2 μm into the surface of the wafer. The substrate was then lapped to a thickness of about 6 mils. Contact (FIG. 2E; layers 36 and 37) to the *n* and *p* surfaces of the wafer was made by conventional evaporation techniques whereby layers of chromium and then gold of several thousand angstroms thickness were applied. The resultant structure was then cut and cleaved to form a number of diodes which were mounted on holders adapted with means for contacting both the *n* and *p* sides of the structures.

The resultant laser diodes were mounted in a microscope fitted for observation of infrared light and were actuated by a pulsed power supply. At room temperature the threshold current density of a laser diode made from this wafer was 3900 A/cm^2.

Utilizing similar techniques, other diodes with the narrow band gap region less than 1.0 μm thick exhibited room temperature thresholds as low as 3000 A/cm^2. Moreover, fully internally reflecting diodes exhibited room temperature thresholds in the range 2300—2800 A/cm^2.

WHAT WE CLAIM IS:—

1. A method of growing a multilayer semiconductor crystal structure in a crystal growth apparatus having a seed holder and a plurality of containers for source solutions comprising the steps of inserting a seed of a group III—V compound semiconductor, applying the seed to a first container in which is a source solution comprising a first group III element, a second group III element and the compound dissolved therein,

rinsed with deionized water, and etch-polished with a bromine - methanol solution to remove surface damage.

Four solutions were then prepared in the following manner. First, the following quantities of materials were weighed out. For solution I, 1 gm Ga, 100 mg, GaAs (undoped), 2 mg Al and 15 mg Sn. For solution II, 1 gm Ga, 100 mg GaAs (undoped) and 1 mg Si. For solution III, 1 gm Ga, 50 mg GaAs (undoped), 3 mg Al and 5 mg Zn. For solution IV, 1 gm Ga, 75 mg GaAs (undoped) and 32 mg Ge. For each solution the Ga plus GaAs was briefly preheated to 900°C under H_2 in a graphite solution holder. The seed and the four prepared solutions of Ga plus GaAs were placed in their respective wells in the apparatus of FIG. 3A. The remainder of the solid components which had been weighed out were then placed into the proper wells with the premixed Ga plus GaAs and were mechanically forced under the surface of the liquid Ga to ensure good contact upon subsequent heating. The holder assembly was then placed into a fused silica tube as illustrated in FIG. 3A. Hydrogen was passed through the tube to flush out air. After flushing for about 10 minutes the tube containing the holders was placed into the furnace which was at 870°C. The auxiliary heater, which consisted of a single loop of about 2 feet of 20 mil nichrome wire heated by 20 volts a.c., was on during this operation. The temperature as measured by the thermocouple was allowed to rise to about 870°C and then a cooling rate of 3°C/minute was established. At 850°C the solution holder was moved so that solution I came into contact with the seed. A mechanical vibrator was used to agitate the solution slightly while cooling to 830°C occurred. At 830°C the solution holder was moved so that solution II covered the seed and remained there with vibration for about 15 seconds. The solution holder was then again moved so that the seed was disposed under the solution III, where it was held for 30 seconds (with vibration). The solution holder was then again moved so that the seed was placed under solution IV and kept there for 60 seconds (with vibration), following which the seed holder 114 was moved again so that the close fitting upper graphite surface 115*b* of solution holder 115 wiped the residual of solution IV from the seed. During this entire procedure the cooling rate of 3°C/minute was maintained. Following the last step the tube was removed from the furnace and allowed to cool to room temperature. This procedure resulted in a wafer 31 of n - type GaAs upon which were deposited, epitaxially, four layers as shown in FIG. 2E. The first layer 32 on the substrate 31 is estimated to consist of n-$Ga_{1-x}Al_xAs$ with x approximately 0.3—0.5, doped by Sn to about 10^{18} electrons/cm^3. An n-n heterojunction 31*a* was formed at the interface between layers 31 and 32. The second layer 33 was GaAs doped by Si (and possibly Zn from diffusion from the following layer) compensated, but p - type. A p-n heterojunction 32*a* was formed at the interface between layers 32 and 33. The third layer 34 was estimated to be p-$Ga_{1-x}Al_xAs$ with x approximately in the range 0.3—0.5 doped p - type by Zn in the range of 10^{18}—10^{19} holes/cm^3. A p-p heterjunction 33a was located at the interface between layers 33 and 34. The fourth layer 35 was GaAs doped p - type by Ge to about 10^{18} holes/cm^3. This resulted in another p-p heterojunction 34*a* between layers 34 and 35.

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WHAT WE CLAIM IS:—

1. A method of growing a multilayer semiconductor crystal structure in a crystal growth apparatus having a seed holder and a plurality of containers for source solutions comprising the steps of inserting a seed of a group III—V compound semiconductor, applying the seed to a first container in which is a source solution comprising a first group III element, a second group III element and the compound dissolved therein,

* C L M S *

controlling the temperature so as to grow a first epitaxial layer thereon, providing relative movement between the holder and the containers so as to apply the seed and first layer to a second container in which is a source solution comprising the said first element and said compound dissolved therein with or without said second element, which, if present, is in a smaller percentage than in the first solution, and regulating the temperature so as to grow a second epitaxial layer having a thickness of 1.5 μ or less on the first layer, the composition of the solutions being such that the first layer is a wide band-gap layer and the second layer is a narrow band-gap layer and further providing relative movement between the holder and a third container, in which is a source solution comprising the first element, the second element in a greater percentage than in the second solution and the compound dissolved therein and further regulating the temperature so as to grow a third layer, the third layer forming a wide band-gap layer from the third solution over the narrow band-gap layer.

2. A method according to claim 1, wherein the thickness of the second epitaxial layer is less than 1.0 μ.

3. A method according to claim 1 or 2 including the step of establishing a temperature gradient such that the portions of the solutions to be contacted by the seed are at a higher temperature than that part of the solutions remote from the seed.

4. A method according to claim 1, 2 or 3 including the step of agitating the solution in contact with the seed.

5. A method according to any preceding claim wherein the containers are in the form of wells in a container member, the seed holder forming a base member to the said wells, including the step of sliding the container member or the seed holder so that the seed contacts the base of each well in turn.

6. A method according to claim 5 wherein the seed holder is provided with means for removing contaminant material from the solution surface at the base of the wells.

7. A method according to any preceding claim wherein the first element is gallium, the second element is aluminium and the compound is gallium arsenide, the solution temperature being within the range 700°C to 1100°C.

8. A method according to any one of claims 1 to 6 wherein the first element is gallium, the second element is aluminium and the compound is gallium phosphide.

9. A method according to claim 7 wherein the first source solution contains an n - type dopant, the second source solution contains at least one dopant sufficient to produce substantially compensated doping in the narrow band-gap layer, and the third source solution includes a p - type dopant so that the resulting semiconductor structure forms a double heterostructure diode having a first wide band-gap layer, a narrower band gap second layer, a p-n heterojunction at the interface between the first and second layers, and a wide band gap third layer with a p-p heterojunction between it and the second layer

10. A method according to claim 7 or 9, wherein each of the source solutions is saturated with arsenic.

11. A method according to claim 9 or 10 wherein the first solution comprises tin, silicon or tellurium as a dopant.

12. A method according to claim 9, 10 or 11 wherein the compensating dopant of the second solution is silicon or silicon and zinc.

13. A method according to any one of claims 9 to 12 wherein the p - type dopant of the third source solution consists of zinc.

14. A method according to any one of claims 9 to 13 including the step of producing relative motion between the crystal holder and the containers so as to apply a fourth source solution to the seed crystal and the first, second, and third layers, the fourth solution consisting of gallium, gallium arsenide and a p - type dopant and controlling the temperature so as to provide a fourth epitaxial layer to serve as a low resistance electrical contact to the structure.

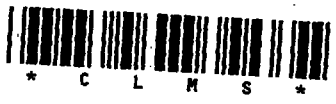
15. A method according to claim 14 wherein the p - type dopant is zinc or germanium.

16. A method according to claim 15 wherein the seed crystal is of gallium arsenide having a carrier concentration in the range 10^{17} to 10^{19} electrons per cubic centimetre, the second solution comprises gallium and gallium arsenide with silicon as the p - type dopant, the solutions being such that resultant structure comprises a first epitaxial layer of composition n-$Ga_{1-x}Al_xAs$, a second epitaxial layer of p-GaAs, a third epitaxial layer of p-$Ga_yAl_{1-y}As$ and a fourth epitaxial layer of p-GaAs and is usable as a double heterostructure semiconductor junction laser, the p-p heterojunction between the second and third epitaxial layers being separated from the p-n heterojunction by a distance of less than a diffusion length of minority carriers.

17. A method of growing a multilayer semiconductor crystal substantially as hereinbefore described with reference to the accompanying drawings.

18. A multilayer semiconductor crystal produced in accordance with the method of any one of claims 1 to 15 or claim 17.

19. A multilayer semiconductor laser crystal produced in accordance with the method of claim 16.



20. A multilayer semiconductor waveguide structure produced in accordance with the method of any one of claims 1 to 15 or claim 17.

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