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(54) IMPROVEMENTS IN OR RELATING TO SEMICONDUCTOR
 LUMINESCENT DEVICES AND METHODS OF MAKING THEM

(71) We, WESTERN ELECTRIC COMPANY, INCORPORATED, of 195 Broadway, New York City, New York State, a Corporation, organised 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 semiconductor devices, and methods of making them, more particularly to electro-luminescent semiconductor devices, i.e., devices which can emit light in response to applied voltages.

In the prior art, P-N junction semiconductor diode devices have been made to emit light in response to forward applied voltage. Such devices are called "electroluminescent" or "light emitting" diodes. For example, in U.K. Patent No. 1,211,358, a P-N junction gallium phosphide diode containing isoelectronic nitrogen traps is described which emits green light under forward voltage applied thereto. As explained in that patent, nitrogen traps (which are isoelectronic with respect to the phosphorus component of gallium phosphide) serve as recombination centres for electrons and holes, thereby emitting green light. However, the light emitting efficiency of such a diode is rather low; and it would therefore be desirable to provide a diode which can emit green light with improved efficiency.

According to one aspect of the invention a semiconductor device comprises a III—V compound semiconductor body including two portions forming a P-N junction and having in at least one portion for a distance of a few diffusion lengths of minority

carriers from the junction a region in which the concentration of nitrogen traps isoelectronic with respect to a component of the semiconductor is substantially greater than in the remainder of that portion, the body being such that electroluminescence is obtained by the application of a suitable voltage across the portions. Thus the diode is built having a relatively high concentration of isoelectronic traps within a neighbourhood of a few diffusion lengths on at least one side of the P-N junction, and a relatively low concentration of such traps in regions more remote from the junction elsewhere in the semiconductor. In this diode, the light emitted near the junction in the high concentration region of traps is transmitted through the remainder of the semiconductor with minimal absorption, thereby improving the luminescent efficiency. Moreover, the bulk electrical conductivity in regions more removed from the junction is advantageously made higher than in the neighbourhood of the junction, in order to minimise heating losses.

According to another aspect of the invention a method of making an electroluminescent III—V compound semiconductor body comprises the steps of solution growing on at least a part of a semiconductor substrate of one conductivity type an epitaxial layer of the same conductivity type having a thickness of a few diffusion lengths of minority carriers both the layer and the substrate containing isoelectronic nitrogen traps, the substrate having a higher electrical conductivity and a greater thickness than the layer and having a concentration of isoelectronic nitrogen traps at least an order of magnitude less than the layer, solution growing on the

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first layer a second epitaxial layer having a conductivity type opposite thereto and a thickness of a few diffusion lengths of minority carriers, solution growing on the second epitaxial layer a third epitaxial layer of the same conductivity type as the second layer and of thickness greater than the second layer, the third layer having a higher electrical conductivity than the second layer, the layers being such that the body when formed and subjected to a suitable voltage across it will emit light.

In a particular embodiment of the invention, a gallium phosphide electroluminescent diode, having a desired concentration profile of isoelectronic nitrogen traps is fabricated by solution epitaxial growth. Upon a relatively thick N-type substrate of gallium phosphide, containing a low concentration of isoelectronic nitrogen traps, a relatively thin N-type epitaxial layer having a thickness of a few diffusion lengths of minority carriers is grown by solution growth. By a low concentration of isoelectronic nitrogen traps means no more than 10^{18} traps per cm^3 , and advantageously below 10^{16} traps per cm^3 . The epitaxial growth of the thin N-type layer is advantageously performed on a clean surface of the substrate by tipping thereon a saturated solution of gallium phosphide in molten gallium containing sulphur and nitrogen impurities. The sulphur furnishes donor impurity levels in the N-type epitaxial layer, while the nitrogen furnishes isoelectronic traps of the order of 10^{19} per cm^3 or more. Next, a thin epitaxial layer of P-type gallium phosphide is solution grown on the exposed surface of the thin N-type epitaxial layer. Again, for this purpose, a solution growth tipping technique is employed using a saturated solution of gallium phosphide in molten gallium containing zinc and nitrogen as impurities. The zinc furnishes acceptor impurity levels in the P-type epitaxial layer, while again the nitrogen furnishes isoelectronic traps. Finally, a thick epitaxial layer of P-type gallium phosphide is solution grown on the exposed surface of the thin P-type epitaxial layer. For this purpose, again a solution growth technique is employed, but in the absence of nitrogen. Ohmic contacts and wire leads are then attached to the thick P-type epitaxial layer and to the N-type substrate, for external electrical connection.

In growth of the above-described epitaxial layers, the thickness of each layer and the resulting concentration profile of significant conductivity determining impurities can be controlled by selection of the operating parameters including temperatures and cooling rates.

This invention can be better understood from the following detailed description when read in conjunction with the drawing which

illustrates diagrammatically an electroluminescent semiconductor device.

The drawing shows an electroluminescent device 10 to be described below in greater detail, in accordance with the invention. Forward voltage of about 2 to 3 volts is applied to the device 10 by a battery 21 through a switch 22. Utilisation means 20 collects the optical radiation 19 emitted by the device when the switch 22 is closed.

The device 10 is composed of a substrate monocrystalline layer 11 of N-type conductivity gallium phosphide, typically about 50 to 75 microns in thickness (z direction), which is relatively free from nitrogen traps (i.e., a concentration of nitrogen traps below 10^{18} per cm^3 and advantageously below 10^{16} per cm^3). Advantageously, the N-type conductivity of the layer 11 is due to a doping concentration of sulphur or other suitable donor impurities of about 5×10^{17} per cm^3 . An epitaxial layer 11.5, about 3 microns thick, is deposited on the layer 11. This layer 11.5 also is N-type conductivity gallium phosphide, but it has a concentration of isoelectronic nitrogen traps of about 1×10^{19} per cm^3 and a concentration of sulphur donor impurities of about 1×10^{17} per cm^3 . Another epitaxial layer 12.5, about 3 microns thick, is deposited on the epitaxial layer 11.5. This layer 12.5 is P-type conductivity gallium phosphide, due to doping with a concentration of about 5×10^{17} zinc or other suitable acceptor impurities per cm^3 . In addition, the layer 12.5 contains of the order of 10^{19} isoelectronic nitrogen traps per cm^3 . An epitaxial P-type layer 12, about 25 microns thick, is deposited on the layer 12.5. This layer 12 advantageously is also relatively free from nitrogen traps (i.e., below 10^{18} per cm^3) and advantageously below 10^{16} per cm^3) and is more strongly P-type than the layer 12.5, due to a concentration of zinc or other suitable acceptor impurity to a level of about 10^{18} per cm^3 at the exposed surface of this layer 12.

The electroluminescent device 10 typically has a cross section of about 5×10^{-4} cm^2 in the xy plane, and is mounted on suitable electrically conducting metal headers 13.1 and 13.2. Ohmic contact is made to the N-type layer 11 typically by means of a tin alloy contact 14 and a gold wire 15 soldered thereto; and ohmic contact is made to the P-type zone 11 typically by means of a gold (2% zinc) alloy wire 16. Absorption of emitted light by poorly reflecting surfaces is prevented by the use of a glass base 17 upon which the headers 13.1 and 13.2 are constructed. Typically, the glass base 17 is 0.06 inches square and 0.01 inches thick. The device 10 is cemented to this glass base 17 by means of a suitable resin layer 18 having a refractive index for

the emitted light which aids in the emergence of the emitted light beam 19.

As further illustrated in the Figure, the metal headers 13.1 and 13.2 are connected through the battery 21 and the switch 22 to complete an electrical circuit including the electroluminescent device 10.

In order to fabricate the device 10, the N-type crystal substrate 11 (doped with 5×10^{17} sulphur donor impurities per cm^3) is formed by conventional methods, such as a pulling technique, or solution epitaxial growth. The epitaxial layer 11.5 is then grown on the substrate 11, advantageously by a solution epitaxial growth technique as follows. The (111) phosphorous face of the substrate 11 is polished and etched, to provide a clean surface for epitaxial growth, and placed at one end of a suitable boat, typically a pyrolytically fired graphite boat enclosed in a quartz tube. At the opposite end of the boat from the crystal substrate 11 is inserted a charge (mixture) of typically about 2 cm gallium and 0.2 gm gallium phosphide. The entire assembly is heated to an elevated temperature, typically about 1050°C in a hydrogen gas ambient containing traces of sulphur. These traces of sulphur are conveniently provided by an auxiliary furnace containing lead sulphide at about 100°C . In addition, the hydrogen gas ambient contains about $1/10\%$ ammonia from an ammonia source to provide the required nitrogen traps. Advantageously, this ambient gas is at a slight positive pressure, to minimize the effects of any leaks. The charge and the substrate are kept separated until thermal equilibrium is attained. The ammonia and the sulphur thereby dissolve and react with the saturated molten gallium growth solution. The boat is then tipped so that this molten gallium solution flows over the substrate 11. Then the substrate 11 is cooled in a period of about 5 minutes by about 5°C , and the boat containing the substrate and growth solution is then rapidly removed from the furnace to quench any further growth. Thereby, the epitaxial layer 11.5 is formed with a thickness of about 3 microns. Next, the epitaxial layer 12.5 is grown by a solution growth method using the same parameter previously used for the growth of the epitaxial layer 11.5, except that instead of the lead sulphide as a source of the (donor) impurity sulphur, a heated source of the acceptor impurity zinc, typically at a temperature of about 660°C , is used to furnish zinc atoms in the hydrogen gas ambient (which also includes $1/10\%$ ammonia). Finally, the epitaxial layer 12 is grown on the layer 12.5 by tipping onto the layer 12.5 another saturated solution of gallium phosphide in gallium which is free of nitrogen, but which also contains the zinc impurities. This tipping is performed at a

temperature of about 1040°C , and then the system is cooled to 900°C in a period of about 15 to 30 minutes before quenching. Thereby, the layer 12 will be formed having a zinc acceptor impurity concentration varying from about 7×10^{17} per cm^3 at the interface with layer 12.5 to about 10^{19} per cm^3 in the final growth of the exposed surface portion.

As an alternative to the above-described two-layer growth of the layers 12.5 and 12, a single layer growth technique can be used in which immediately after the growth of the layer 12.5 (i.e., after the 5°C cooling), the cooling cycle is interrupted to permit shutting off the ammonia (nitrogen) source and evaporation of the gallium nitride from the growth solution. Then the cooling cycle is resumed in the absence of nitrogen and the zinc doped layer 12 is formed.

Various other Group II donor impurities such as tellurium or selenium can be used instead of sulphur; various other Group II acceptor impurities such as cadmium can be used instead of zinc; and other type Group III-V semiconductors can be used instead of gallium phosphide, for example, gallium nitride. Finally, only a single one of the layers 11.5 or 12.5 need contain the nitrogen traps, at some sacrifice of efficiency.

WHAT WE CLAIM IS:—

1. A semiconductor device comprising a III-V compound semiconductor body including two portions forming a P-N junction and having in at least one portion for a distance of a few diffusion lengths of minority carriers from the junction a region in which the concentration of nitrogen traps isoelectronic with respect to a component of the semiconductor is substantially greater than in the remainder of that portion, the body being such that electroluminescence is obtained by the application of a suitable voltage across the portions.
2. A device according to claim 1 wherein the body is of gallium phosphide.
3. A device according to claim 2 in which the N-type portion of the body is sulphur doped.
4. A device according to claim 2 wherein the P-type portion of the body is zinc doped.
5. A device according to claim 1 wherein the concentration of nitrogen traps in the said regions is substantially 10^{19} per cubic centimetre and in the remainder of said portion is not greater than 10^{18} per cubic centimetre.
6. A device according to claim 1 wherein the body is of gallium nitride.
7. A device according to claim 1, 2 or 6 wherein the N-type portions contain tellurium or selenium as significant impurity.
8. A device according to claim 1, 2, 6 or 130

the emitted light which aids in the emergence of the emitted light beam 19.

As further illustrated in the Figure, the metal headers 13.1 and 13.2 are connected through the battery 21 and the switch 22 to complete an electrical circuit including the electroluminescent device 10.

In order to fabricate the device 10, the N-type crystal substrate 11 (doped with 5×10^{17} sulphur donor impurities per cm^3) is formed by conventional methods, such as a pulling technique, or solution epitaxial growth. The epitaxial layer 11.5 is then grown on the substrate 11, advantageously by a solution epitaxial growth technique as follows. The (111) phosphorous face of the substrate 11 is polished and etched, to provide a clean surface for epitaxial growth, and placed at one end of a suitable boat, typically a pryoritically fired graphite boat enclosed in a quartz tube. At the opposite end of the boat from the crystal substrate 11 is inserted a charge (mixture) of typically about 2 cm gallium and 0.2 gm gallium phosphide. The entire assembly is heated to an elevated temperature, typically about 1050°C in a hydrogen gas ambient containing traces of sulphur. These traces of sulphur are conveniently provided by an auxiliary furnace containing lead sulphide at about 100°C . In addition, the hydrogen gas ambient contains about $1/10\%$ ammonia from an ammonia source to provide the required nitrogen traps. Advantageously, this ambient gas is at a slight positive pressure, to minimize the effects of any leaks. The charge and the substrate are kept separated until thermal equilibrium is attained. The ammonia and the sulphur thereby dissolve and react with the saturated molten gallium growth solution. The boat is then tipped so that this molten gallium solution flows over the substrate 11. Then the substrate 11 is cooled in a period of about 5 minutes by about 5°C , and the boat containing the substrate and growth solution is then rapidly removed from the furnace to quench any further growth. Thereby, the epitaxial layer 11.5 is formed with a thickness of about 3 microns. Next, the epitaxial layer 12.5 is grown by a solution growth method using the same parameter previously used for the growth of the epitaxial layer 11.5, except that instead of the lead sulphide as a source of the (donor) impurity sulphur, a heated source of the acceptor impurity zinc, typically at a temperature of about 660°C , is used to furnish zinc atoms in the hydrogen gas ambient (which also includes $1/10\%$ ammonia). Finally, the epitaxial layer 12 is grown on the layer 12.5 by tipping onto the layer 12.5 another saturated solution of gallium phosphide in gallium which is free of nitrogen, but which also contains the zinc impurities. This tipping is performed at a

temperature of about 1040°C , and then the system is cooled to 900°C in a period of about 15 to 30 minutes before quenching. Thereby, the layer 12 will be formed having a zinc acceptor impurity concentration varying from about 7×10^{17} per cm^3 at the interface with layer 12.5 to about 10^{18} per cm^3 in the final growth of the exposed surface portion.

As an alternative to the above-described two-layer growth of the layers 12.5 and 12, a single layer growth technique can be used in which immediately after the growth of the layer 12.5 (i.e., after the 5°C cooling), the cooling cycle is interrupted to permit shutting off the ammonia (nitrogen) source and evaporation of the gallium nitride from the growth solution. Then the cooling cycle is resumed in the absence of nitrogen and the zinc doped layer 12 is formed.

Various other Group II donor impurities such as tellurium or selenium can be used instead of sulphur; various other Group II acceptor impurities such as cadmium can be used instead of zinc; and other type Group III-V semiconductors can be used instead of gallium phosphide, for example, gallium nitride. Finally, only a single one of the layers 11.5 or 12.5 need contain the nitrogen traps, at some sacrifice of efficiency.

WHAT WE CLAIM IS:—

1. A semiconductor device comprising a III-V compound semiconductor body including two portions forming a P-N junction and having in at least one portion for a distance of a few diffusion lengths of minority carriers from the junction a region in which the concentration of nitrogen traps isoelectronic with respect to a component of the semiconductor is substantially greater than in the remainder of that portion, the body being such that electroluminescence is obtained by the application of a suitable voltage across the portions.
2. A device according to claim 1 wherein the body is of gallium phosphide.
3. A device according to claim 2 in which the N-type portion of the body is sulphur doped.
4. A device according to claim 2 wherein the P-type portion of the body is zinc doped.
5. A device according to claim 1 wherein the concentration of nitrogen traps in the said regions is substantially 10^{19} per cubic centimetre and in the remainder of said portion is not greater than 10^{18} per cubic centimetre.
6. A device according to claim 1 wherein the body is of gallium nitride.
7. A device according to claim 1, 2 or 6 wherein the N-type portions contain tellurium or selenium as significant impurity.
8. A device according to claim 1, 2, 6 or 130



7 wherein the P-type portions contain cadmium as significant impurity.

9. A device according to any preceding claim wherein the said variation of concentration of traps is present in both portions.

10. A method of making an electroluminescent semiconductor body according to claim 1 comprising the steps of solution growing on at least a part of a semiconductor substrate of one conductivity type an epitaxial layer of the same conductivity type having a thickness of a few diffusion lengths of minority carriers both the layer and the substrate containing isoelectronic nitrogen traps, the substrate having a higher electrical conductivity and a greater thickness than the layer and having a concentration of isoelectronic nitrogen traps at least an order of magnitude less than the layer, solution growing on the first layer a second epitaxial layer having a conductivity type opposite thereto and a thickness of a few diffusion lengths of minority carriers, solution growing on the second epitaxial layer a third epitaxial layer of the same conductivity type as the second layer and of thickness greater than the second layer, the third layer having a higher electrical conductivity than the second layer, the layers being such that the body when formed and subjected to a suitable voltage across it will emit light.

11. A method according to claim 10 wherein the third layer has a concentration of isoelectronic nitrogen traps that is at least an order of magnitude below that of the first and second layers.

12. A method according to claim 10 or 11 wherein the substrate material is N-type gallium phosphide having a concentration of nitrogen traps less than 10^{16} per cubic centimetre and a net concentration of significant donor impurities of sulphur of the order of 10^{17} per cubic centimetre.

13. A method according to claim 10, 11 or 12 wherein the first layer is grown from a saturated solution of gallium phosphide in gallium in the presence of sulphur forming the donor impurity and nitrogen.

14. A method according to claim 13 wherein the second layer is grown from a saturated solution of gallium phosphide in gallium in the presence of zinc forming the acceptor impurity and of nitrogen.

15. A method according to claim 14 wherein the third layer is grown from a saturated solution of gallium phosphide in gallium with zinc as the acceptor impurity.

16. A semiconductor device substantially as herein described with reference to and as shown in the drawing.

17. A method of making a semiconductor device substantially as herein described with reference to the drawing.

18. A device made in accordance with the method of any one of claims 10 to 15 or 17.

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