

[54] **FABRICATING A GALLIUM PHOSPHIDE DEVICE**

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 342,371, March 19, 1973, abandoned.

Foreign Application Priority Data

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[51] Int. Cl..... **H01b 7/38**

[58] Field of Search..... **148/171-173, 148/189; 252/623 GA; 317/235 AN**

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[57] **ABSTRACT**

With the method of this invention a layer of gallium phosphide is formed of liquid phase epitaxy. In this invention an N-type gallium phosphide substrate and a melt of gallium-gallium phosphide solution are disposed in a boat which is inserted in a quartz tube. The melt also contains oxygen and zinc which form a recombination center pair for red emission. Zinc is supplied as a vapor phase with carrier gas. The zinc concentration of the melt and vapor equilibrate with each other and the zinc concentration of the melt is selected in consideration of the distribution coefficient of zinc and the electron concentration of the N-type substrate. The substrate is then flooded with the melt and an epitaxial layer is deposited. The zinc is diffused into the epitaxial layer and gives it P-type conductivity, but it is not diffused into the substrate so much that a zinc-oxygen pair exists in the vicinity of a P-N junction. It improves the red emission efficiency of a gallium phosphide luminescent diode.

12 Claims, 4 Drawing Figures

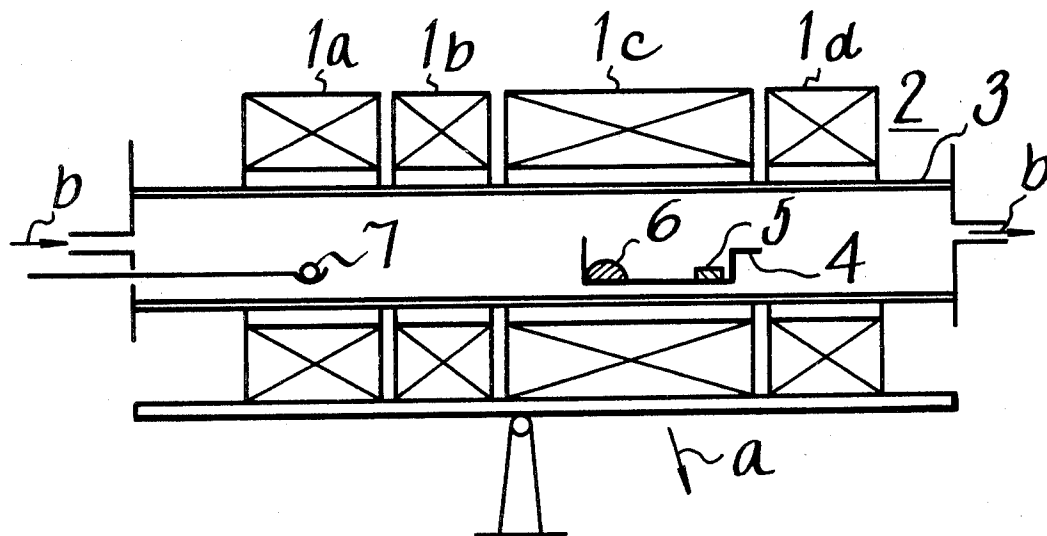


Fig. 1

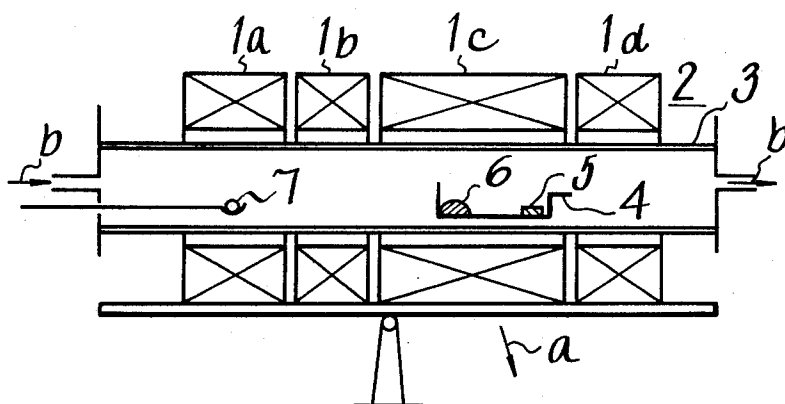


Fig. 2

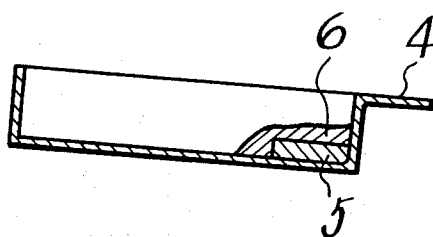


Fig. 3

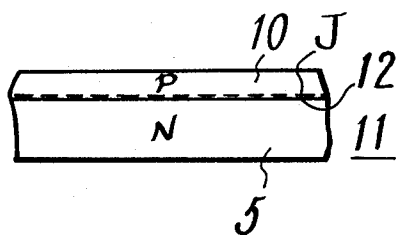
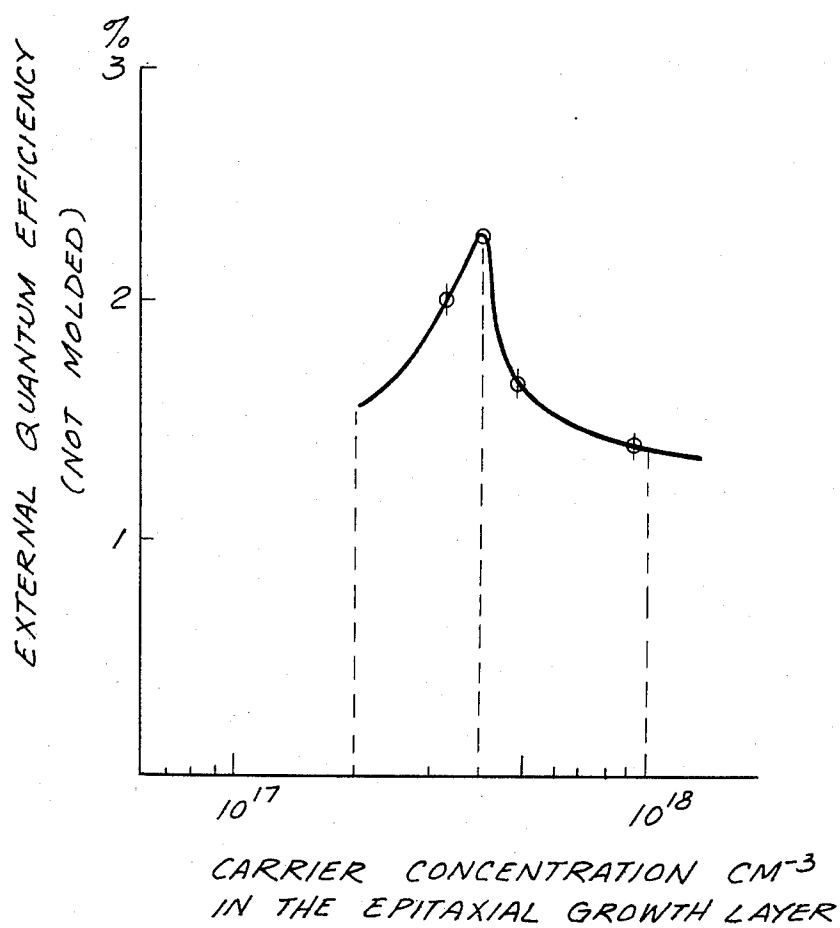


Fig. 4

FABRICATING A GALLIUM PHOSPHIDE DEVICE

RELATED APPLICATION

The present invention is a continuation-in-part application of my copending application, Ser. No. 342,371, filed Mar. 19, 1973, now abandoned and an improvement over that described in United States application, Ser. No. 236,695, filed Mar. 21, 1972, assigned to the same assignee, and of which I am a co-inventor.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates generally to a method of making a gallium phosphide device and more particularly to a liquid phase epitaxy method which improves the light emission efficiency of a luminescent diode made of a semiconductor such as gallium phosphide.

2. Description of the Prior Art

In general, in order to increase the light emission efficiency of a gallium phosphide luminescent semiconductor device and to increase the red emission efficiency thereof, it is necessary to provide a pair of atoms, for example, zinc (Zn) which may become an acceptor [or cadmium (Cd)] and a donor of deep level, such for example, as oxygen (O). In the case of increasing the green emission efficiency it is necessary to permit existence of nitrogen (N) in the vicinity of the P-N junction. In this case it is also necessary to so select the number of the pair of oxygen (O) and zinc (Zn) or cadmium (Cd) and that of nitrogen (N) that their concentration is sufficiently high in the vicinity of P-N junction.

It is further desired in the prior art, so as to fabricate a semiconductor device with high reproducibility.

As a method of fabricating a luminescent semiconductor device of gallium phosphide, there has been proposed a diffusion method and a liquid phase epitaxial method. However, a device made by the diffusion method has the disadvantage that flaws and distortion appear in its P-N junction to deteriorate its light emission efficiency, while a device made by the liquid phase epitaxial method has the disadvantage that the concentration of the acceptor in the vicinity of its P-N junction is difficult to control. This is caused by the fact that in the case where, for example, zinc (Zn) and oxygen (O), the zinc (Zn) diffuses more quickly than the oxygen (O).

SUMMARY OF THE INVENTION

It is an object of this invention to provide an improved method of fabricating a luminescent semiconductor device such as a gallium phosphide luminescent diode.

It is a further object of this invention to provide a liquid epitaxial method of fabricating a luminescent semiconductor device from gallium phosphide in which the concentration of an acceptor therein can be accurately controlled, resulting in a very high light emission efficiency.

According to this invention, a crystalline substrate of N-type gallium phosphide, with tellurium, for example, added thereto, and a gallium-gallium phosphide solution are disposed in a heating reaction furnace, and thereafter zinc (Zn) and cadmium (Cd), by way of example, are doped into a melt of the solution as an acceptor impurity with a predetermined concentration,

and finally the melt is flooded over the N-type substrate and cooled to form a P-type epitaxial growth layer on the N-type substrate. In this case, the amount of the acceptor impurity in the melt is selected so that the concentration of the acceptor impurity in the epitaxial growth layer will be equal to or lower than that of the N-type impurity in the N-type substrate, and the concentration doped into the melt is selected to be in equilibrium or approximate equilibrium with that of the P-type impurity in the epitaxial phase.

With the method according to this invention, the acceptor is doped into the melt of gallium-gallium phosphide solution which is used to form an epitaxial growth layer on the substrate, with equilibrium concentration or almost equilibrium concentration, so that the amount of the doped acceptor can be selected stably and with high reproducibility. The doping concentration or the equilibrium concentration for determining this doping concentration can be controlled by selecting the concentration of an acceptor impurity (Zn) in a carrier gas, of the flow rate of the carrier gas, the heating temperature and so on, so that the doping amount can be stably and positively selected to be sufficiently low.

Further, a luminescent semiconductor device manufactured according to this invention has the acceptor concentration in a P-type layer lower than the carrier concentration in an N-type substrate, so that a P-N junction can be formed on a boundary between a substrate and an epitaxial growth layer having oxygen (O) as a donor of deep level. Hence a pair of zinc (Zn) as an acceptor and oxygen (O) in the donor of deep level can be presented in the vicinity of the P-N junction. As a result, the light emission efficiency of the luminescent semiconductor device can be increased.

Other objects, features and advantages of this invention will be apparent from the following description taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic cross-sectional view of an example of apparatus used for practicing the method according to this invention;

FIG. 2 is an enlarged cross-sectional view for illustrating a liquid epitaxial process;

FIG. 3 is an enlarged partial cross-sectional view for illustrating an embodiment of gallium phosphide luminescent semiconductor substrate manufactured by this invention;

FIG. 4 is a graph of quantum efficiency as a function of carrier concentration.

DESCRIPTION OF THE PREFERRED EMBODIMENT

This invention will be described hereinbelow, by way of example, with reference to the drawings.

In FIG. 1, reference numeral 2 generally designates a heating furnace which comprises a plurality of heating furnace units; namely first to fourth heating furnace units 1a, 1b, 1c and 1d arranged sequentially as shown in the figure. The first furnace unit, 1a, is used for vaporizing an acceptor impurity and the third furnace unit, 1c, is used for carrying out an epitaxial growth. The second furnace unit, 1b, acts as an auxiliary furnace unit for controlling the first furnace unit, 1a, in a manner to prevent variation of the temperature distribution therein which might be caused by the increase

of temperature in the third furnace unit, 1c, and the fourth furnace unit 1d, is also an auxiliary furnace to control the third furnace unit, 1c, to maintain a uniform temperature distribution.

A quartz tube 3 is disposed within the first to fourth furnace units, 1a to 1d, and a boat 4 is inserted into the quartz tube 3 at the position corresponding to the third furnace unit, 1c. A single crystalline substrate of N-type gallium phosphide (GaP) 5, is located in the boat 4 at one end thereof, while a gallium-gallium phosphide solution 6 is disposed in the boat 4 at the opposite end thereof from the substrate 5. The gallium-gallium phosphide (Ga-GaP) solution 6 contains, for example, 10 grams of gallium (Ga), 1 gram of gallium phosphide (GaP) and 0.2 grams of gallium trioxide (Ga₂O₃) for an oxygen source, at room temperature.

The third furnace unit, 1c, is heated to 950°C. and the first furnace unit, 1a, is also heated to 500° to 570°C. An impurity source 7, for example, zinc (Zn) as an acceptor impurity is inserted into the tube 3 at the position corresponding to the first furnace unit 1a. A carrier gas such, for example, as argon (Ar) is then supplied into the tube 3 in the direction as shown in FIG. 1 by arrows b to continuously supply zinc vapor from the source 7 to a melt of the Ga-GaP solution 6 in the boat 4 with this carrier gas. Thus, zinc (Zn) is dissolved sufficiently into the melt 6. While Zn vapor is being supplied to the melt 6 with the carrier gas, the third furnace 1c is heated to an epitaxial treating temperature of 1,050°~1,150°C., for example, 1,100°C. In this case, Zn is dissolved in the melt 6 in such amount that its concentration substantially reaches the equilibrium concentration at that temperature. In other words, the Zn is dissolved in the melt 6 in such amount that the partial pressure of Zn in the melt 6 reaches equilibrium with the vapor pressure of Zn in the carrier gas. In this case, according to Raoult's law, the concentration of Zn in the solution 6, $R_a(Zn)$, is given by

$$R_a(Zn) = P(Zn) / P_o(Zn) \quad (1)$$

where $P(Zn)$ and $P_o(Zn)$ are the zinc partial pressure in the furnace and the vapor pressure of pure zinc at the epitaxy temperature, respectively. The equilibrium concentration can be set by selecting the concentration of Zn in the carrier gas and the heating temperature of the melt 6.

The solution 6 containing therein the acceptor, i.e., the zinc (Zn) and the donor of deep level, i.e., oxygen (O) is caused to flow over the substrate 5 and cover it, by inclining the furnace 2 in the direction shown by an arrow a in FIG. 1, and inclining the boat 4 as shown in FIG. 2. Thereafter, the third furnace unit 1c is gradually lowered in temperature to form the gallium phosphide (GaP) semiconductor layer 10 on the substrate 5 in an epitaxial growth manner. The Ga-GaP solution remaining on the epitaxial growth layer 10 is removed, for example, by wiping it away. In this case, the zinc concentration incorporated into the epitaxial growth layer 10 is expressed by

$$N(Zn) = k \cdot R_a(Zn) \cdot \rho_{GaP} / M_{GaP} \cdot N, \quad (2)$$

where k is the distribution coefficient, N is the Avogadro Number and ρ_{GaP} and M_{GaP} are the density and the

molecular weight of GaP, respectively. In the doping range from 10^{17} to slightly above 10^{18} cm^{-3} the difference between the carrier gas and zinc concentrations is small, so the carrier concentration in the epitaxial growth layer 10 can also be expressed by Eq. (2). Therefore, if the concentration $R_a(Zn)$ is selected so that the zinc concentration $N(Zn)$ is equal to or less than the carrier concentration of the N-type substrate 5, an epitaxial growth layer 10 formed on the N-type substrate 5 is of P-type and the P-N junction J never penetrates into the substrate 5 through the boundary 12.

By forming an electrode on the upper surface of the P-type region, i.e., the epitaxial growth layer 10, of a semiconductor base body 11 and also an electrode on the lower surface of the N-type region or substrate 5 of the body 11, a luminescent diode is obtained. If desired, this luminescent diode may be divided into plural ones to obtain a plurality of luminescent diodes.

With the method according to this invention, the acceptor is doped into the gallium-gallium phosphide (Ga-GaP) solution, is used to form the epitaxial growth layer 10 on the substrate 5, has an equilibrium concentration, or almost equilibrium concentration, as mentioned above, so that the amount of the doped acceptor can be selected stably and with high reproducibility. As shown by the Eq. (1), the doping amount, or equilibrium concentration for determining this doping amount, can be selected low enough by selecting the proper concentration of the acceptor impurity Zn in the carrier gas, or by adjusting suitably the flow rate of the carrier gas, the heating temperature, etc., so that the doping amount can be stably and positively selected sufficiently low.

As resulting from Eq. (2), the doping amount $R_a(Zn)$ of Zn in the melt 6 should be selected equal to or less than $n_d / 2.486 \times 10^{-20} \text{ mol \%}$, where $n_d (\text{cm}^{-3})$ is a carrier concentration of the substrate 5 in order not to form a P-N junction in the substrate 5.

With the method of this invention described above, the concentration of the acceptor (the Zn) in the melt of Ga-GaP solution 6, which is used for the liquid epitaxial, is selected so low that when the melt 6 is flooded over the substrate 5 for the epitaxial growth, any worry that the Zn in the melt 6 may be diffused into the substrate 5 which would result in the P-N junction being formed in the region of the substrate 5 with almost no oxygen (O) to deteriorate the light emission efficiency of the device, is avoided due to the fact that the diffusion speed of Zn is higher than that of oxygen (O). As mentioned above, the P-N junction J is formed on the boundary 12 between the substrate 5 and the epitaxial growth layer 10 and this epitaxial growth layer 10 is of P-type conductivity and with the Zn in a predetermined concentration.

The luminescent semiconductor device made by the method of this invention has an acceptor concentration in the P-type layer lower than that of the carrier in the N-type substrate, so that the P-N junction J is formed between the substrate 5 and the epitaxial growth layer 10 having oxygen (O) as the donor of deep level and hence a pair of zinc (Zn) as the acceptor and oxygen (O) as the donor of deep level is present in the vicinity of the P-N junction J. As a result, the light emission efficiency of the luminescent semiconductor device is increased.

FIG. 4 shows the quantum efficiencies of the luminescent semiconductor devices of this invention as a function of the carrier concentration in the epitaxial growth layer. An optimum carrier concentration is about $4 \times 10^{17} \text{ cm}^{-3}$ regardless of the carrier concentration in the substrate, while an optimum range of the carrier concentration in the layer is from $2 \times 10^{17} \text{ cm}^{-3}$ to 10^{18} cm^{-3} . Therefore, carrier concentrations in the substrate may be selected preferably between $2 \times 10^{17} \text{ cm}^{-3}$ and 10^{18} cm^{-3} to obtain a luminescent semiconductor device of high light emission efficiency by this invention.

With the method of this invention, when the Zn is doped into the melt of the Ga-GaP solution, the Zn vapor is simultaneously supplied to the substrate 5. In this case, however, the amount of the Zn vapor is selected low as to make the doping amount of Zn into the melt of Ga-GaP solution also low, so that even if the diffusion of Zn into the substrate 5 takes place, the Zn concentration in the substrate 5 is selected so that an acceptor concentration in the epitaxial growth layer 10 is lower than the carrier concentration in the substrate 5 (i.e., the donor concentration) with the result that there is no fear that the substrate 5 is partially changed to P-type conductivity. Accordingly, it will be understood that even if the diffusion mentioned above takes place, the P-N junction J is not formed in the substrate 5.

The following table shows the amount of Zn vapor and the partial pressure of Zn in the melt of the Ga-GaP solution for the condition where argon (Ar) is supplied to the quartz tube 3 as a carrier gas at a flow rate of 350 $\text{cm}^3/\text{min.}$, and the third furnace unit 1c is held at a temperature of 1,100°C.

Table

Amount of Zn vapor	Partial Pressure of Zn		
0.4(mg/min.)	0.392×10^{-3}	(Atmospheric Pressure)	(0.298mmHg)
0.6(mg/min.)	0.587×10^{-3}	do.	(0.446mmHg)
0.8(mg/min.)	0.783×10^{-3}	do.	(0.595mmHg)
1.0(mg/min.)	0.979×10^{-3}	do.	(0.744mmHg)
2.0(mg/min.)	1.958×10^{-3}	do.	(1.488mmHg)
2.7(mg/min.)	2.643×10^{-3}	do.	(2.009mmHg)
4.0(mg/min.)	3.916×10^{-3}	do.	(2.976mmHg)
5.0(mg/min.)	4.895×10^{-3}	do.	(3.720mmHg)

If the flow rate of Zn vapor is selected to be 1 mg/min. (0.744 mm Hg), the Zn concentration in the P-type epitaxial growth layer 10 becomes $n = 4.5 \times 10^{17} \text{ cm}^{-3}$. If the flow rate of the Zn vapor is selected to be 0.6 mg/min. (0.446 mmHg), the Zn concentration in the layer 10 becomes $n = 2.2 \times 10^{17} \text{ cm}^{-3}$. Accordingly, if a substrate having a carrier concentration of $5 \times 10^{17} \text{ cm}^{-3}$ is used as the substrate 5, there is no danger that the P-N junction J will be formed in the substrate 5. If the carrier concentration in the substrate 5 is selected to be $5 \times 10^{17} \text{ cm}^{-3}$ and the flow rate of the Zn vapor is selected higher than 2.7 mg/min. (2.009 mmHg), the acceptor concentration thus formed in the epitaxial growth layer 10 becomes higher than $1 \times 10^{18} \text{ cm}^{-3}$. Thus, there may occur the danger that the P-N junction will be formed in the substrate 5 by diffusion, which is undesirable. If the carrier concentration of the substrate 5 is selected in the order of $1 \times 10^{18} \text{ cm}^{-3}$, the flow rate of the Zn vapor should be selected to be 0.6~1.0 mg/min. (0.446~0.744 mmHg) to cause the

acceptor concentration of the epitaxial growth layer 10 to be $2 \sim 5 \times 10^{17} \text{ cm}^{-3}$. Thus, a luminescent semiconductor device with high light emission efficiency can be obtained with high reproducibility.

The light emission efficiency of the luminescent semiconductor device manufactured according to this invention becomes 2~3% in mean value with a non-resin mold but 3~4% with a transparent resin mold. In this case, an N-type substrate with a carrier (i.e., electron) concentration of $2 \sim 10 \times 10^{17} \text{ cm}^{-3}$ is used as the substrate, the partial pressure of Zn is selected to be $0.35 \times 10^{-3} \sim 2.5 \times 10^{-3}$ atmospheric pressure. On the other hand, if the partial pressure of Zn is selected to be 2.643×10^{-3} atmospheric pressure, the light emission efficiency of the device thus obtained becomes 1.5% with a non-resin but 2% with a transparent resin mold. If the partial pressure of Zn is selected higher than that mentioned above, the light emission efficiency in mean value becomes about 0.5% with no mold. The mean light emission efficiency of a GaP luminescent diode on market is about 1~2% with a transparent resin mold. The mean light emission efficiency of a luminescent semiconductor device, which is obtained by this invention with the condition that the partial pressure of Zn is selected $0.35 \sim 2.5 \times 10^{-3}$ atmospheric pressure, is 2~3% with a resin mold similar to that of a device on market.

As will be apparent from the foregoing description, a GaP luminescent diode high in light emission efficiency can be obtained by this invention with high reproducibility.

A modification of the above described invention may be had where oxygen is doped into the melt of Ga-GaP solution from the first by adding thereto gallium trioxide (Ga_2O_3). It is also possible for the oxygen to be doped into the melt of Ga-GaP solution by supplying Ga_2O gas with the carrier gas. (See U.S. Pat. No. 3,689,330).

It is also possible that cadmium (Cd) may be used as the P-type impurity instead of Zn.

Further, in place of argon, hydrogen gas may be used (for N-type dope) as a carrier gas for green light emission, nitrogen gas for red light emission and so on.

The method wherein the carrier gas is continuously supplied to the quartz tube 3 (so-called open tube type) is described in the foregoing, but a so-called closed tube type method may be employed in this invention with similar results.

It will be apparent to those skilled in the art that many variations and changes could be effected without departing from the spirit and scope of the novel concepts of this invention as defined by the appended claims.

I claim as my invention:

1. A method of fabricating a gallium phosphide device comprising the steps of:

- providing a substrate of N-type gallium phosphide;
- forming a melt of gallium-gallium phosphide solution including a P-type impurity, said impurity having a concentration that maintains approximately equilibrium with that of the ambient vapor phase; and
- growing a P-type epitaxial layer on said substrate from said melt, said impurity concentration therein being not more than $n_d/2.486 \text{ k} \times 10^{-20} \text{ mol } \%$ wherein $n_d \text{ (cm}^{-3}\text{)}$ is the carrier concentration in

said substrate and k is a distribution coefficient of said impurity.

2. A method in accordance with claim 1, wherein said substrate contains tellurium as an N-type impurity.

3. A method in accordance with claim 1, wherein said melt also contains oxygen.

4. A method in accordance with claim 3, wherein said oxygen is supplied from gallium trioxide.

5. A method in accordance with claim 3, wherein said impurity is selected from the group consisting of zinc and cadmium to form a recombination center with said oxygen.

6. A method in accordance with claim 1, wherein said melt further contains nitrogen to form a recombination center.

7. A method in accordance with claim 1, wherein a P-N junction is formed substantially between said substrate and said epitaxial layer so that a recombination center exists near said junction.

8. A method of fabricating a gallium phosphide device in a heating furnace through which a quartz tube extends which comprises:

a. causing a carrier gas to flow as a stream through said tube from one end to the other;

b. placing a boat within said tube;

c. placing an N-type gallium phosphide substrate in said boat at the downstream end thereof;

d. placing a melt of gallium-gallium phosphide having gallium trioxide therein in the upstream end of said boat;

e. vaporizing zinc into said carrier gas upstream of the boat;

f. maintaining the temperature of the melt at a point where the zinc vapor is dissolved in the melt in such an amount that the partial pressure of zinc in the melt reaches equilibrium with the vapor pressure of zinc in the carrier gas, an amount of zinc therein in the equilibrium state being selected equal to or lower than $n_d/2.486 k \times 10^{-20}$ mol %, wherein n_d (cm^{-3}) is the concentration of the N-type impurity in the substrate and k is a distribution coefficient of said zinc; and

g. thereafter causing the melt containing acceptor impurity of zinc and donor impurity of deep level oxygen to overflow the gallium phosphide substrate to form an epitaxial growth layer thereon.

9. A method in accordance with claim 8, wherein the furnace maintains the melt at a temperature between $1,050^\circ\text{C}$. and $1,150^\circ\text{C}$. at the time it is caused to overflow the substrate.

10. A method in accordance with claim 8, wherein the furnace maintains the melt at a temperature of approximately $1,100^\circ\text{C}$. at the time it is caused to overflow the substrate.

11. A method in accordance with claim 9, wherein the temperature of the furnace in the region of said substrate is maintained at approximately 950°C . before the coating step and wherein the zinc is vaporized at approximately 500°C . to 570°C .

12. A method in accordance with claim 11, wherein the carrier gas has a rate of flow of approximately $350 \text{ cm}^3/\text{min}$.

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