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(54) IMPROVEMENTS IN OR RELATING TO SEMICONDUCTOR DEVICES

(71) We, WESTERN ELECTRIC COMPANY, INCORPORATED, of 195 Broadway, New York City, New York State, United States of America, 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 in particular to a means of extending the operating life of light emitting p-n junction devices. In the context of this application it should be understood that the term "light emitting p-n junction devices" includes both incoherent light emitting (electroluminescent) and coherent light emitting (laser) devices.

Electroluminescent diodes in particular have recently been the subject of extensive research and development. Due to their small size, efficiency, fast response time and economy of manufacture, they are particularly suited for numeric and alpha-numeric displays in a wide variety of applications. Laser diodes show potential in optical communications and memory device applications especially in view of the recent development of continuous wave laser diodes operating at room temperatures (British Patent Specification No. 1342767).

One persistent difficulty regarding the use of these light emitting diodes has been the fact that over a period of time light output decreases under forward bias and eventually the diode must be replaced. The lifetime of the best devices is of the order of a few years. This is indeed a significant improve-

ment over the prior art filament bulbs. However, when the diodes are incorporated into apparatus which must be utilized and serviced in the field (e.g., a telephone), it is desirable to extend this lifetime to at least that of the incorporating apparatus in order to avoid the substantial expense of replacement.

Scattered attempts have been made to increase the lifetime of GaAs diodes by means of some kind of surface coating. For example, a coating of silicon oxide produced some improvement in the degradation of GaAs at low current densities (Lanza et al, "Aging Effects in GaAs Electroluminescent Diodes", *Solid State Electronics*, Vol. 10, p. 21 (1967)). However, the improvement was negligible under operating conditions, which required high current densities.

The precise mechanism of degradation of light emitting p-n junction devices remains unknown. The current weight of authority, however, holds that degradation under operating conditions is due primarily to a bulk phenomenon, i.e., the diffusion of interstitial atoms within the bulk of the junction regions. (See, for example, Stainer and Anderson, "Degradation of GaAs Injection Devices", *Solid State Electronics*, Vol. 11, pp. 65-86 (1968)). Thus it was generally concluded that surface treatment of the devices could not have any appreciable effect in extending the lifetime of the devices.

In spite of this, a passivation technique has been discovered which extends the operating life of light emitting diodes. Accordingly, the invention provides a method of treating a light emitting semiconductor p-n junction device, wherein the device containing gallium has grown thereover a film containing gallium

oxide by immersing in an aqueous oxidizing reagent, wherein the film is at least 100 Å thick and wherein the device is baked to expel excess moisture from the film so that the operating life of the light emitting p-n junction device is extended.

Typically the diodes are p-n junction devices containing a gallium compound. In particular, the method of the present invention involves the formation of an amorphous, native gallium oxide containing layer on the surface of the device. The device is immersed in an aqueous oxidizing system and then dried. The resulting oxide layer chemically passivates the device by preventing the transport of impurities into the bulk material, in particular, into the region of the p-n junction. The expected room temperature half-life of diodes so treated is in excess of 10^6 hours. An overcoating of a glassy dielectric material may also be provided to enhance passivation.

A specific embodiment of the invention will now be described by way of example and with reference to the accompanying drawings, in which:—

Fig. 1 is a cross-section of a device treated in accordance with the present embodiment;

Fig. 2 is a graph showing the degradation characteristics in a nitrogen ambient of devices treated in accordance with one embodiment of the invention in comparison with untreated devices;

Fig. 3 is a graph showing the degradation characteristics in air of two groups of devices treated in accordance with the present embodiment, one including in addition a silicon dioxide deposition, in comparison with a group of untreated devices, and

Fig. 4 is a graph showing the degradation characteristics of three groups of devices, one treated in accordance with the present embodiment, one untreated, and one coated with silicon dioxide.

Fig. 1 shows a typical gallium phosphide light emitting diode which has been treated according to the present embodiment of the invention. The device 10 comprises an n-type bulk region, 11, an n-type tellurium-doped layer, 12, grown therein by liquid phase epitaxy, and a p-type zinc and oxygen doped layer, 13, also grown by liquid phase epitaxy. The diode is then bonded on the *n* side to a suitable mounting, 14, and an ohmic contact, 15, is formed on the *p* side. Wire leads (not shown) are then provided for connection to a desired circuit. After mounting and formation of the ohmic contact, a thin layer 16 containing gallium oxide is grown on the remaining exposed surface of the diode to provide passivation. The oxide layer may be about 300–400 Å thick, and therefore, it may be desirable to include an additional passivating layer 17, of a glassy, dielectric

material such as silicon dioxide formed on the oxide layer.

It will be appreciated that the diode may not be as shown but may for example be formed in a mesa structure and beam-leaded rather than wire bonded. Instead of liquid phase, epitaxy, the junction may be formed by diffusion techniques. In addition, the structure may include more than one junction as in a pnpn latching device.

The oxide layer 16 is formed by immersing the assembled diode in an aqueous oxidizing system such as a solution of hydrogen peroxide. The concentration of hydrogen peroxide utilized for GaP was 30 percent although a range of typically 10–70 percent would be useful. The solution is held near the boiling point. The device is removed from the solution when a layer of gallium oxide a few hundred angstroms thick is formed. A minimum thickness of approximately 100 Å would be needed. For a 30 percent solution, the device is immersed for approximately seven hours.

It is significant to note that while others have been used a hydrogen peroxide solution in various etching processes, apparently no one has produced this form of stable, amorphous gallium oxide. Prior work has produced crystalline forms of gallium oxide at much higher temperatures. (See, for example, Rubenstein, "The Oxidation of GaP and GaAs", *Journal of Electrochemical Society*, Vol. 113, No. 6, pp. 540–542).

The amorphous film as grown, does not passivate. Excess water must be removed by appropriate drying. In general, a heat treatment consisting of a successively increasing temperature up to approximately 150–350° C during a period of one-half hour to five hours in a dry non-corrosive ambient e.g., an inert gas such as nitrogen is satisfactory. In particular, the device may be heated in a nitrogen atmosphere for approximately three hours at successive temperatures of 95° C and 250° C.

Tests were performed to determine the effect of the passivating oxide layer on the degradation characteristics of the GaP diode. In the test all the diodes were formed from a single slice of liquid encapsulated Czochralski grown n-type GaP. A liquid phase epitaxial tellurium-doped layer was formed thereon, followed by forming a p-type zinc and oxygen doped layer on the Te-doped layer. The wafer was slurry cut and the diode chips were bonded to headers using Si—Au preforms. Ohmic contacts for the *p*-regions were obtained with Be—Au contacts and wire bonding. The devices were then etched in a solution of H_2SO_4 , H_2O and H_2O_2 to remove all surface damage due to cutting. Subsequent rinsing in distilled, deionized water and then in isopropanol ensured clean surfaces.

A group of these diodes were then passivated according to the present embodiment by immersing in a 30 percent hydrogen peroxide solution at a temperature of approximately 100° C for seven hours. These devices were then dried at temperatures successively increased to 250° C. for approximately three hours in a nitrogen atmosphere. Another group of diodes was left untreated.

Fig. 2 is a plot of the normalized external quantum efficiency (η/η_0) on a natural log scale, as a function of time T in hours for a group of five oxidized diodes and a group of five unoxidized diodes aged at 200° C. and 10 mA forward current in a nitrogen ambient. The points plotted are the mean values for the diodes within a group. As clearly demonstrated by the graph, the group of diodes oxidized and annealed at 250° C. according to line 18 exhibit a marked reduction in degradation as compared to the unoxidized diodes according to line 19. Furthermore, the group of oxidized diodes exhibits a far greater uniformity in degradation as indicated by the vertical error bars showing one standard deviation from the mean. Removal of the oxide film from three passivated, partially degraded diodes resulted in extremely rapid and erratic degradation as shown in the graph by line 20.

Further tests were performed to determine the nature of the degradation process. Current voltage characteristics for the same GaP diode before and after oxidation were measured. The curves were shown to be substantially the same indicating that surface recombination centres were not affected by the oxidation process. After degradation, the characteristics were complicated by an excess current component, but electroluminescent time decay remained unchanged demonstrating that radiative recombination mechanisms were not affected by degradation. The rate of degradation of unoxidized diodes was shown to increase considerably after heat treatment.

On the basis of these tests, it is theorized that degradation is due to the transport of impurities from the surface of the device to the junction region resulting in a decrease in the injection efficiency. The oxide formed on the periphery of the device according to the present embodiment prevents these impurities from diffusing into the region of the p-n junction by binding them at the surface and/or acting as a barrier to the formation of impurities from the atmosphere on the surface.

The room temperature half-life of these GaP diodes was estimated on the basis of an activation energy of 0.93 eV previously determined for a group of hermetically sealed GaP diodes. Preliminary data on the passivated diodes compares favourably to the data on hermetically sealed diodes and so the use

of this activation energy presents a reasonable approximation. In this manner, a GaP diode treated in accordance with the present invention is estimated to possess a half-life of 10^8 — 10^9 hours.

Since the oxide layer is relatively thin (usually 300—400 Å), the passivation characteristics may be increased by forming an overcoating of silicon dioxide. This is done by a standard silane treatment, i.e., reacting silane with oxygen at a temperature of between 300 and 600° C and allowing the resulting silicon dioxide to deposit on the amorphous oxide layer. The resulting layer is a glassy, dielectric material which apparently functions as an additional barrier to contaminants in the air. It is considered that other glassy materials may be used for the same purpose.

Fig. 3 is a graph of normalized external quantum efficiency on a natural log scale as a function of time T in hours for three groups of GaP diodes. One group was oxidized according to the method described above, a second group was similarly oxidized and further treated with silane at 350° C. and the third group was left unoxidized. The diodes were aged at 200° C, 10 mA forward current in an air ambient. It will be appreciated that the degradation for the oxidized diodes treated with SiO_2 according to line 21 was superior to that for the diodes according to line 22 (i.e., those not treated with SiO_2). However, both sets of diodes were markedly superior to those diodes unoxidized according to line 23. This demonstrated the fact that the deposition of an overcoating of silicon dioxide further increases the lifetime of the diodes and also lends support to the theory that degradation is slowed by the formation of a barrier to outside contaminants. The data also shows however that the treated diodes will behave as well under ordinary atmospheric conditions as in a nitrogen ambient.

Similar tests have indicated that the silane treated diodes will exhibit a more appreciable improvement over the oxidized diodes when aged at higher temperatures.

It is important to note that while the gallium oxide containing layer alone and the combination of gallium oxide containing and silicon dioxide layers greatly improve the lifetime of the diodes, apparently the silicon dioxide layer alone will not be effective. Fig. 4 is again a plot of normalized quantum efficiency η/η_0 as a function of time T in hours for three groups of GaP diodes. One group 24 was oxidized in accordance with the present embodiment, another group 25 was unoxidized, and a third group was unoxidized 26 but treated with silane at a temperature of 375° C.

It can easily be seen that the silane treatment alone is not effective in inhibiting de-

gradation. The reason the silane treated diodes exhibit even greater degradation than the unoxidized diodes is apparently that the high annealing associated with this treatment promotes defect generation in the junction region and therefore enhances impurity transport from the surface.

It was discovered that thick oxides may be achieved by including a catalyst in the H_2O_2 oxidizing system. This catalyst may be one of the noble metals such as silver, platinum, gold or palladium, or alloys thereof. To demonstrate the catalytic action three slices of n-type GaP were immersed in separate solutions of boiling H_2O_2 for approximately seven hours. One system had no catalyst, one had a solid piece of platinum in the solution, and one had a piece of gold which was bonded to one surface of the sample. The uncatalyzed solution produced an oxide approximately 75 Å thick, the platinum containing solution produced an oxide 125 Å thick, and the solution containing gold bonded to the sample produced an oxide 700 Å thick. Clearly, then, the addition of the catalyst to the system enhanced the growth rate of the oxide. This is apparently the result of the decomposition of the H_2O_2 by the catalyst. The bonding of the catalyst to the sample, however, produced such an extraordinary increase in the growth rate, suggesting that an additional mechanism is involved here. Apparently the gold, which does not oxidize, keeps a path open for electron transfer between the solution and the semiconductor which would otherwise be closed by the oxide growing on the entire surface area of the sample. Therefore, use of a gold alloy as the ohmic contact on the final devices, as described in relation to Fig. 1, results in a catalytic enhancement of the oxidation rate when the device is treated according to the present invention.

It will be appreciated that while the present embodiment of the invention has been described in terms of oxidizing GaP diodes by reacting with a hydrogen peroxide solution, the invention is not so limited. It appears that any p-n junction light emitting device containing appreciable amounts of gallium (i.e., at least 5 percent) will form the same passivating oxide film. For example, the invention is applicable to devices comprising GaAs, GaAlAs, GaAsP, AlGaP, InGaAs or InGaP and mixtures thereof. Furthermore, the oxidizing system may take many forms other than hydrogen peroxide. This was confirmed by reacting two slices of n-type tellurium-doped GaAs with water

at room temperature and 60° C, respectively.

However, it was noted that free carrier concentration influences the oxidation rate of GaAs in water. Experiments showed that oxidation in boiling water of n-type GaAs doped at $2 \times 10^{17} \text{ cm}^{-3}$ produced an oxide only about 50—100 Å thick in five hours. Therefore, a minimum doping density of approximately $2 \times 10^{17} \text{ cm}^{-3}$ is required to produce films of useful thickness in reasonable time periods. Light emitting devices containing an oxide produced by boiling water were subsequently baked to expel excess moisture therefrom and to extend the operating life of the devices.

WHAT WE CLAIM IS:—

1. A method of treating a light emitting semiconductor p-n junction device, wherein the device containing gallium has grown thereover a film containing gallium oxide by immersing in an aqueous oxidizing reagent, wherein the film is at least 100 Å thick and wherein the device is baked to expel excess moisture from the film so that the operating life of the light emitting p-n junction device is extended.

2. A method as claimed in claim 1, wherein the aqueous solution is hydrogen peroxide having a concentration of 10 to 70 percent.

3. A method as claimed in claim 1 or claim 2, wherein the device comprises GaP, GaAs, GaAsP, GaAlAs, AlGaP, InGaAs or InGaP.

4. A method as claimed in any one of claims 1—3, wherein the oxidizing reagent is water and in which the device contains a doping density of at least $2 \times 10^{17} \text{ cm}^{-3}$.

5. A method as claimed in any one of the preceding claims, wherein the film is from 300—400 Å thickness.

6. A method as claimed in any one of the preceding claims, wherein the device is baked at progressively increasing temperatures up to 350° C in an inert atmosphere.

7. A method as claimed in any one of the preceding claims, wherein the film containing gallium oxide is coated with a glassy dielectric material.

8. A method as claimed in claim 7, wherein the dielectric material is a silicon dioxide layer.

9. A method as claimed in any one of the preceding claims, wherein the film is grown in the presence of a catalyst.

10. A method as claimed in claim 10, wherein the catalyst is contained in the oxidizing reagent or is bonded to a surface of the device.

11. A method as claimed in claim 9 or

gradation. The reason the silane treated diodes exhibit even greater degradation than the unoxidized diodes is apparently that the high annealing associated with this treatment promotes defect generation in the junction region and therefore enhances impurity transport from the surface.

It was discovered that thick oxides may be achieved by including a catalyst in the H_2O_2 oxidizing system. This catalyst may be one of the noble metals such as silver, platinum, gold or palladium, or alloys thereof. To demonstrate the catalytic action three slices of n-type GaP were immersed in separate solutions of boiling H_2O_2 for approximately seven hours. One system had no catalyst, one had a solid piece of platinum in the solution, and one had a piece of gold which was bonded to one surface of the sample. The uncatalyzed solution produced an oxide approximately 75 Å thick, the platinum containing solution produced an oxide 125 Å thick, and the solution containing gold bonded to the sample produced an oxide 700 Å thick. Clearly, then, the addition of the catalyst to the system enhanced the growth rate of the oxide. This is apparently the result of the decomposition of the H_2O_2 by the catalyst. The bonding of the catalyst to the sample, however, produced such an extraordinary increase in the growth rate, suggesting that an additional mechanism is involved here. Apparently the gold, which does not oxidize, keeps a path open for electron transfer between the solution and the semiconductor which would otherwise be closed by the oxide growing on the entire surface area of the sample. Therefore, use of a gold alloy as the ohmic contact on the final devices, as described in relation to Fig. 1, results in a catalytic enhancement of the oxidation rate when the device is treated according to the present invention.

It will be appreciated that while the present embodiment of the invention has been described in terms of oxidizing GaP diodes by reacting with a hydrogen peroxide solution, the invention is not so limited. It appears that any p-n junction light emitting device containing appreciable amounts of gallium (i.e., at least 5 percent) will form the same passivating oxide film. For example, the invention is applicable to devices comprising GaAs, GaAlAs, GaAsP, AlGaP, InGaAs or InGaP and mixtures thereof. Furthermore, the oxidizing system may take many forms other than hydrogen peroxide. This was confirmed by reacting two slices of n-type tellurium-doped GaAs with water

at room temperature and 60° C, respectively.

However, it was noted that free carrier concentration influences the oxidation rate of GaAs in water. Experiments showed that oxidation in boiling water of n-type GaAs doped at $2 \times 10^{17} \text{ cm}^{-3}$ produced an oxide only about 50–100 Å thick in five hours. Therefore, a minimum doping density of approximately $2 \times 10^{17} \text{ cm}^{-3}$ is required to produce films of useful thickness in reasonable time periods. Light emitting devices containing an oxide produced by boiling water were subsequently baked to expel excess moisture therefrom and to extend the operating life of the devices.

WHAT WE CLAIM IS:—

1. A method of treating a light emitting semiconductor p-n junction device, wherein the device containing gallium has grown thereover a film containing gallium oxide by immersing in an aqueous oxidizing reagent, wherein the film is at least 100 Å thick and wherein the device is baked to expel excess moisture from the film so that the operating life of the light emitting p-n junction device is extended.

2. A method as claimed in claim 1, wherein the aqueous solution is hydrogen peroxide having a concentration of 10 to 70 percent.

3. A method as claimed in claim 1 or claim 2, wherein the device comprises GaP, GaAs, GaAsP, GaAlAs, AlGaP, InGaAs or InGaP.

4. A method as claimed in any one of claims 1–3, wherein the oxidizing reagent is water and in which the device contains a doping density of at least $2 \times 10^{17} \text{ cm}^{-3}$.

5. A method as claimed in any one of the preceding claims, wherein the film is from 300–400 Å thickness.

6. A method as claimed in any one of the preceding claims, wherein the device is baked at progressively increasing temperatures up to 350° C in an inert atmosphere.

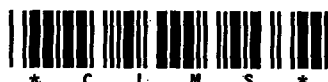
7. A method as claimed in any one of the preceding claims, wherein the film containing gallium oxide is coated with a glassy dielectric material.

8. A method as claimed in claim 7, wherein the dielectric material is a silicon dioxide layer.

9. A method as claimed in any one of the preceding claims, wherein the film is grown in the presence of a catalyst.

10. A method as claimed in claim 10, wherein the catalyst is contained in the oxidizing reagent or is bonded to a surface of the device.

11. A method as claimed in claim 9 or



* C L M S *

claim 10, wherein the catalyst is a noble metal or an alloy thereof.

12. A method as claimed in claim 1 substantially as hereinbefore described with reference to and illustrated in the accompanying drawings.

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