

PATENT SPECIFICATION (11)

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(54) IMPROVEMENTS IN OR RELATING TO A METHOD OF TREATING A GALLIUM-CONTAINING COMPOUND SEMICONDUCTOR

(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:—

The invention relates to treating a gallium-containing compound semiconductor so as to produce thereon an adherent oxide layer.

Growth of a stable amorphous native oxide on gallium-containing compounds has been observed recently and is, for example, discussed in British Patent Application No. 55273/71 (Serial No. 1,360,073). The importance of this oxide film has been demonstrated in the field of light-emitting p-n junction devices. When the oxide is grown on the surface of the device, the operating life of the device is significantly increased.

The method hitherto employed to produce the oxide involves immersing the device in a hot oxidizing solution such as H_2O_2 for a period of several hours until a film a few hundred Angstroms thick is observed. It will be appreciated that this is a fairly slow process. It has also been observed that when the carrier concentration of certain semiconductor materials such as GaAs is too low, oxidation may occur even more slowly if at all.

Thus, while the prior art method is adequate, it is generally desirable to speed the oxidation process to facilitate commercial production. It is also desirable to make the oxidation essentially independent of the doping of the semiconductor material. Finally, if a method could be provided which produced much thicker native oxides than possible under the present method, the oxide could be used to perform other functions

generally associated with insulating material in integrated circuit technology, for example, impurity diffusion masking, insulating from beam lead contacts and forming metal-oxide-compound semiconductor structures.

Accordingly, the invention provides a method of treating a gallium-containing compound semiconductor comprising making the compound semiconductor an anode in an electrolytic cell wherein the electrolyte is either water having a pH of from 1—5 or from 9—13 or an aqueous solution of hydrogen peroxide having a pH of from 1—6 or 8—13 and passing an electric current through the electrolytic cell so as to produce an adherent oxide layer on the compound semiconductor.

These and other objects are achieved in accordance with the invention which involves producing the amorphous oxide layer by means of certain electrolytic systems. A self-limiting growth process may be established by applying a constant potential to the system and allowing the current through the electrolytic cell to decrease asymptotically to some predetermined value.

In a particular embodiment employing an H_2O_2 solution at room temperature, an oxide thickness of several thousand Angstroms was produced in 30 minutes on a GaP sample.

A specific method of treating a gallium-containing compound semiconductor embodying the invention will now be described by way of example and with reference to the accompanying drawings, in which:—

Fig. 1 is a schematic drawing showing an electrolytic oxidation system in accordance with one embodiment of the invention;

Fig. 2 is a graph of current (I) in milliamps through the system of Fig. 1 as a function of time (T) in seconds for several applied potentials; and

Fig. 3 is a graph of the oxide thickness (D) in Angstroms of oxide grown on several samples in accordance with the embodiment

of Fig. 1 as a function of the pH of the electrolyte.

Fig. 1 shows schematically, an electrolytic cell having a container, 10, containing a liquid electrolyte 11. A gallium-containing compound semiconductor material, 12, is immersed in the solution with an electrode, 13, comprising one of the noble metals such as platinum or gold. Coupled to these electrodes (12, 13) is a d.c. current source, 14, and a variable resistance, 15, which together comprise a constant voltage source. The semiconductor material is made the anode and the noble metal the cathode of the electrolytic system. Included in the circuit is an ammeter, 16, for measuring the current through the cell.

The electrolyte is either a hydrogen peroxide and water solution or simply water alone provided that the pH of the latter is adjusted as described below. The H_2O_2 solution is conveniently 30 percent by weight, although a range of 3—90 percent by weight would be useful.

In a particular embodiment, slices of a liquid encapsulated Czochralski grown n-type GaP were chemmechanically polished in a bromine-methanol solution and made the anode of the cell. The electrolyte was a 30 percent by weight aqueous H_2O_2 solution. The cathode was platinum. Electrolytic oxidations were performed for different values of the applied potential at room temperature for a period of approximately 2000 seconds. The slices were then dried by heating to 250°C for approximately three hours in a nitrogen ambient. It was noted that an amorphous form of native oxide was grown on the surface of the samples. The thickness of the oxide layer and the refractive index were measured for each run and the results are reproduced in the following table:

45	Voltage (Volts)	Thickness (Å)	Refractive Index
	10	125	1.70—1.75
	25	300	1.70—1.75
50	50	525	1.68
	100	1230	1.63
	160	3500	1.2

The remarkable growth rate produced by this electrolytic oxidation system will be apparent. Whereas in the prior art chemical system for example, British Patent Application No. 55273/71 (Serial No. 1,360,073) a film thickness of only 300—400 Angstroms is produced after approximately seven hours, in accordance with the present electrolytic process, for example, a film thickness of 3500 Angstroms is produced after approximately 33 minutes with an applied

potential of 160 volts. In addition to the advantage of having a greater oxidation rate, this process results in films which are thick enough to be used in the production of gallium-containing compound semiconductor integrated circuits and to provide the necessary insulation in such circuits.

A useful range of applied potential is approximately 5—175 volts. Higher applied potentials may be employed in the system by using pulsed d.c. potential. For example, it was observed that when 225 volts was supplied, cracks developed in the oxide surface. This problem is avoided by using a pulsed d.c. potential up to 225 volts such that the cell is pulsed on for $\frac{1}{3}$ of a cycle and off for the remaining $\frac{2}{3}$ of a cycle. Such a procedure produced an oxide thickness which gave an interference colour in the purplish range. This indicates a thickness in excess of 4000 Angstroms. The problem may also be avoided by raising the temperature of the electrolyte to near the boiling point. The resulting motion of the solution should prevent depletion of the reagent at the semiconductor interface, provide additional free charged carriers in the GaP, and allow uninhibited growth of the oxide.

If a drying cycle is desired, a useful range appears to be 150—250°C temperature for one-half hour to five hours in a nitrogen atmosphere.

During each oxidation, the current passing through the cell was also measured and the results for each applied potential are reproduced in the graph shown in Fig. 2. The decreasing current demonstrates the fact that the oxide is growing and causing an increasing resistance in the cell. Once the resistivity of the film is measured, therefore, the time required to produce a predetermined oxide thickness can be calculated for each applied voltage. Fig. 2 also suggests that a self-limiting growth process may be established. That is, due to the increased resistance provided by the growing oxide, the current through the cell will decrease asymptotically to some small value, at which time the growth of the oxide will virtually cease. It is expected that this asymptotic value is approximately 10^{-2} milliamperes. It may also be desirable to provide a constant current source rather than a constant voltage source in the system. In such a case, the current would be supplied until the voltage reached a predetermined value for a particular oxide thickness desired.

It should be recognized that although the embodiment of the invention has been described primarily in relation to the oxidation of n-type GaP, the method may be applied to other materials. For example, p-type GaP was oxidized according to the procedure described above and substantially the

same current-time curves were obtained. GaAs may also be oxidized in accordance with this process. For example, an n-type GaAs slice with a carrier concentration of approximately $2 \times 10^{17}/\text{cm}^2$ was made the anode of the same electrolytic system. The electrolyte was again a 30 percent aqueous solution of H_2O_2 . When a constant potential of 100 volts was supplied to the system an oxide approximately 1100 Å thick was grown in just ten minutes. It is important to note that since free carriers are being supplied by the electrolytic system, the lower limit of carrier concentration in GaAs of $2 \times 10^{17}/\text{cm}^2$ which permitted oxidation in the aforesaid British Patent Application No. 55273/71 (Serial No. 1,360,073) is not applicable here.

It was also discovered in the GaAs oxidation systems that the pH of the electrolyte can have a bearing on the growth rate of the oxide. It was found that the standard chemically pure grade H_2O_2 solution used in the above GaAs oxidation had a pH of approximately 3.5. The pH of the solution was decreased to approximately 2 by the addition of 0.2 cc of H_3PO_4 to approximately one-half litre of solution. The oxidation was repeated using a constant potential of 100 volts. After ten minutes, an oxide approximately 1750 Å thick was grown on the slice. Similarly, when the pH was increased by the addition of a suitable source of hydroxyl ions, such as NH_4OH , the growth rate was similarly increased. The results of these experiments are reproduced in the graph of oxide thickness (D) in Angstroms against pH shown in Fig. 3. All oxidations were performed at a constant potential of 100 volts for ten minutes. It was also found that at pH within the range 6—8, etching occurs, i.e., the oxide tends to dissolve in the solution. However, when the pH is raised to within the range 8—13 by the addition of NH_4OH , a stable oxide will again form as when the pH was in the acidic range of from 1—6.

In a further embodiment, GaAs may also be oxidized in an electrolyte of water alone provided that the pH is suitably adjusted. Here, the pH of the solution also has an effect on oxide growth. When slices of n-type GaAs were made in the anode of systems where the electrolyte was water at pH=5—9 and a constant potential of 100 volts was applied, no fall-off in current was observed after approximately ten minutes. This indicates that most of the oxide which was formed was dissolved and so the film was worthless as an insulator or as a barrier to outside contaminants. However, when the pH of the water was lowered to a pH

range of 1—5 by the addition of a source of hydrogen ions such as H_3PO_4 or H_2SO_4 , the system produced oxides which show a current decrease similar to those illustrated in Fig. 2. The same results were achieved when the pH of the water was raised to 9—13 by a source of hydroxyl ions such as NH_4OH . Thus, GaAs may be oxidized electrolytically in a system where water is the electrolyte provided that the pH is adjusted to within the ranges described above.

In general, any semiconductor compound containing an appreciable amount of gallium (i.e., at least 5 percent) will form the amorphous native oxide when treated in accordance with the present embodiment of the invention. Other possible materials include GaAlAs, AlGaP, InGaP, InGaAs and mixtures thereof.

WHAT WE CLAIM IS:—

1. A method of treating a gallium-containing compound semiconductor comprising making the compound semiconductor an anode in an electrolytic cell wherein the electrolyte is either water having a pH of from 1—5 or from 9—13 or an aqueous solution of hydrogen peroxide having a pH of from 1—6 or 8—13 and passing an electric current through the electrolytic cell so as to produce an adherent oxide layer on the compound semiconductor.

2. A method as claimed in claim 1, wherein a constant potential is applied to the cell.

3. A method as claimed in claim 2, wherein the potential is from 5 to 175 volts.

4. A method as claimed in any one of claims 1—3, wherein the hydrogen peroxide electrolyte is a 30 percent by weight solution.

5. A method as claimed in any one of claims 1—4, wherein the electrolyte is heated to a temperature near its boiling point.

6. A method as claimed in claim 1, wherein a pulsed d-c potential is applied to the cell of up to 225 volts.

7. A method as claimed in any one of the preceding claims, wherein the pH of the hydrogen peroxide is adjusted to 8—13 by the addition of NH_4OH .

8. A method as claimed in any one of claims 1—6, wherein the pH of the water is adjusted to 1—5 by the addition of either H_2SO_4 or H_3PO_4 and the pH is adjusted to 9—13 by the addition of NH_4OH .

9. A method as claimed in any one of the preceding claims, wherein the gallium containing semiconductor compound is selected from the group consisting of GaP, GaAs, AlGaP, InGaP and InGaAs.



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same current-time curves were obtained. GaAs may also be oxidized in accordance with this process. For example, an n-type GaAs slice with a carrier concentration of approximately $2 \times 10^{17}/\text{cm}^2$ was made the anode of the same electrolytic system. The electrolyte was again a 30 percent aqueous solution of H_2O_2 . When a constant potential of 100 volts was supplied to the system an oxide approximately 1100 Å thick was grown in just ten minutes. It is important to note that since free carriers are being supplied by the electrolytic system, the lower limit of carrier concentration in GaAs of $2 \times 10^{17}/\text{cm}^2$ which permitted oxidation in the aforesaid British Patent Application No. 55273/71 (Serial No. 1,360,073) is not applicable here.

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In a further embodiment, GaAs may also be oxidized in an electrolyte of water alone provided that the pH is suitably adjusted. Here, the pH of the solution also has an effect on oxide growth. When slices of n-type GaAs were made in the anode of systems where the electrolyte was water at pH=5—9 and a constant potential of 100 volts was applied, no fall-off in current was observed after approximately ten minutes. This indicates that most of the oxide which was formed was dissolved and so the film was worthless as an insulator or as a barrier to outside contaminants. However, when the pH of the water was lowered to a pH

range of 1—5 by the addition of a source of hydrogen ions such as H_3PO_4 or H_2SO_4 , the system produced oxides which show a current decrease similar to those illustrated in Fig. 2. The same results were achieved when the pH of the water was raised to 9—13 by a source of hydroxyl ions such as NH_4OH . Thus, GaAs may be oxidized electrolytically in a system where water is the electrolyte provided that the pH is adjusted to within the ranges described above.

In general, any semiconductor compound containing an appreciable amount of gallium (i.e., at least 5 percent) will form the amorphous native oxide when treated in accordance with the present embodiment of the invention. Other possible materials include GaAlAs, AlGaP, InGaP, InGaAs and mixtures thereof.

WHAT WE CLAIM IS:—

1. A method of treating a gallium-containing compound semiconductor comprising making the compound semiconductor an anode in an electrolytic cell wherein the electrolyte is either water having a pH of from 1—5 or from 9—13 or an aqueous solution of hydrogen peroxide having a pH of from 1—6 or 8—13 and passing an electric current through the electrolytic cell so as to produce an adherent oxide layer on the compound semiconductor.

2. A method as claimed in claim 1, wherein a constant potential is applied to the cell.

3. A method as claimed in claim 2, wherein the potential is from 5 to 175 volts.

4. A method as claimed in any one of claims 1—3, wherein the hydrogen peroxide electrolyte is a 30 percent by weight solution.

5. A method as claimed in any one of claims 1—4, wherein the electrolyte is heated to a temperature near its boiling point.

6. A method as claimed in claim 1, wherein a pulsed d-c potential is applied to the cell of up to 225 volts.

7. A method as claimed in any one of the preceding claims, wherein the pH of the hydrogen peroxide is adjusted to 8—13 by the addition of NH_4OH .

8. A method as claimed in any one of claims 1—6, wherein the pH of the water is adjusted to 1—5 by the addition of either H_2SO_4 or H_3PO_4 and the pH is adjusted to 9—13 by the addition of NH_4OH .

9. A method as claimed in any one of the preceding claims, wherein the gallium containing semiconductor compound is selected from the group consisting of GaP, GaAs, AlGaP, InGaP and InGaAs.



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10. A method of treating a gallium containing compound as claimed in claim 1 and substantially as hereinbefore described with reference to and illustrated in the accompanying drawings.

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