

# PATENT SPECIFICATION

DRAWINGS ATTACHED

986.403

Date of Application and filing Complete Specification Nov. 19, 1962.

No. 43637/62.

Application made in United States of America (No. 153459) on Nov. 20, 1961.

Complete Specification Published March 17, 1965.

© Crown Copyright 1965.



Index at acceptance: —H1 K(1A1, 1CX, 2S1, 2S2, 2S10, 2S20, 3E3, 3J, 3S, 3X); C7 F(1A, 1B2, 2B, 2K, 2Z4, 2Z8, 3C, 3E, 4W, 4X, 5A)

Int. Cl.:—H 01 I/C 23 c

## COMPLETE SPECIFICATION

### Method of Forming P-N Junctions

We, TEXAS INSTRUMENTS INCORPORATED, 13500 North Central Expressway, Dallas, Texas, United States of America, a corporation organized and existing under the laws of the State of Delaware, 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 method of forming P-N junctions in semiconductors and more particularly to a method of forming P-N junctions in semiconductors by epitaxial deposition techniques.

It has been found desirable to extend the substrate for an epitaxially grown device by epitaxial growth of the material thereof having like-type conductivity. This extended or continuation layer of the substrate perfects the substrate surface by allowing the crystal to grow away from the disorder associated at the surface. The continuation layer of the substrate does not have to be of the same resistivity material and may be either of a higher or lower resistivity depending on the ultimate results desired.

It has been found, however, that a minimum thickness of the continuation layer must be grown on the substrate in order to perfect the substrate and provide certain other advantages hereinafter described. Having epitaxially deposited the continuation layer on the substrate of like-type conductivity, various P-N junction diodes, transistors and multi-layered devices may then be fabricated. To avoid contamination of the opposite-type conductivity layer from impurities in the original substrate during epitaxial deposition thereof, the continuation layer of the substrate is deposited in appropriate thicknesses to function as a buffer layer which prevents the substrate impurities from out-diffusing or out-

gassing through the continuation layer and into the opposite-type conductivity layer. 45

The present invention is a method of forming P-N junctions in semiconductors by epitaxial deposition, comprising the steps of subjecting a semiconductor material substrate of one conductivity to a temperature suitable for promoting the epitaxial growth thereof, subjecting said semiconductor substrate at said temperature to a vapour containing a controlled ratio of a first volatilized compound of said semiconductor material and a second volatilized compound of a like-type conductivity-imparting impurity for a period of time to deposit epitaxially a like-type conductivity continuation layer of said semiconductor material on said substrate, and thereafter subjecting said substrate at said temperature to a second vapour containing a controlled ratio of said first volatilized compound and a third volatilized compound of an opposite-type conductivity-imparting impurity for a period of time to deposit epitaxially an opposite-type conductivity layer of said semiconductor material on said continuation layer. 50 55 60 65

Accordingly, by utilizing the invention thin layer collector regions for transistors can be fabricated, greatly reducing the bulk resistance of the collector region without any undesirable changes in the specific collector resistance. Of course, it is necessary to deposit the thin collector region on a very low resistivity single crystal substrate of like-type conductivity as that of the collector region, the substrate being single crystalline to allow epitaxial growth of a collector region. In such a transistor, the substrate supports the collector region. 70 75 80

The invention will now be described, by way of example, with reference to the accompanying drawing, wherein:—

Figure 1 illustrates a P-N junction device 85

having a continuation layer of the substrate on one side of the junction; and

Figure 2 illustrates schematically suitable apparatus for performing the epitaxial deposition process.

Referring now to Figure 1, a silicon P-N junction device is illustrated made according to the present invention. An N+ substrate 40 having an N continuation layer 50 epitaxially deposited thereon and then a P layer 60 epitaxially deposited on the N layer 50 is illustrated. The substrate may have any desired resistivity and could also be P+ or P-type conductivity. As aforementioned, the continuation layer provides a buffer zone to prevent impurities in the substrate from being diffused or out-gassed into the opposite-type conductivity layer 60, deposited on the continuation layer. Hence several factors require consideration in determining the thickness of the continuation layer. These factors include the type of impurity used to dope the original substrate 40, the rate growth of the various epitaxial layers, and the diffusion rate of the various impurities in the semiconductor material. Likewise, the temperature of the substrate and the period of time for epitaxial deposition should be considered to determine what thickness the continuation layer should have to avoid the contamination. Moreover, the doping level of the opposite-type conductivity layer to be epitaxially deposited on the continuation layer affects the thickness of the continuation layer since high doping levels in the opposite-type conductivity layer require higher compensation before degradation is effected.

Suitable apparatus for performing the epitaxial deposition process of the invention is illustrated in Figure 2. A reactor generally designated as 1 is provided having a reactor tube 5 made of quartz or other suitable non-contaminating material for semiconductors, which is surrounded by a furnace 2 to maintain appropriate temperatures within the reactor. A quartz or other noncontaminating material slab 4 is placed within reactor tube 5 and provides support for the semiconductor substrate 3 from which epitaxial semiconductor devices are to be grown. The reactor is provided with an outlet tube 9 contained within a sealing stopper 7, that leads to a gas flare-off (not shown). An inlet tube 8 is provided extending into reactor tube 5 and is held in place by suitable sealing stopper 6.

The input source to the reactor 1 is the effluent from evaporator 10, the evaporator 10 being provided to ensure that liquid 25, being in a controlled ratio of silicon halide to the impurity halide, is completely evaporated and carried by the hydrogen from container 30 into reactor 1. For this purpose, quartz chips 13 are provided in the evaporator and are heated appropriately by heater 14. Drop tube 12 held within the evaporator 10 by

sealing stopper 15, is provided to inject liquid reactants 25 into the hydrogen stream. An inlet 11 is provided in evaporator 10 to maintain countercurrent flow of the hydrogen with respect to the liquid reactants. A hydrogen bottle 30 is provided with an outlet tube 31 and a control valve 18. A flow meter 16 couples the control valve 18 with the inlet 11 and monitors the hydrogen flow. The liquid reactants are provided in container 20. Said container has a liquid outlet tube 21 extending well below the surface of the liquid reactants 25. Also, the container 20 has a pressure cap 23 having an inlet 22 to provide a pressurized inert gas to the liquid reactants 25. The rate of flow of the liquid reactants 25 into drop tube 12 is controlled by flow valve 19 and is monitored by flow meter 17.

In operation, a substrate 3 on which a continuation layer and an opposite-type conductivity layer are to be epitaxially deposited is placed in reaction tube 5, after which the system is adjusted to allow hydrogen flow through evaporator 10 and into reaction tube 5. The reaction tube 5 is then heated to a temperature at which epitaxial deposition takes place. The hydrogen flow over the heated substrate 3 etches the surface and the exhaust is removed to a gas flare-off. After a short period of hydrogen etching, a semiconductor halide and an appropriate impurity as liquid 25 is introduced into the evaporator 10. Heat from element 14 evaporates the liquid 25 in evaporator 10, and hydrogen vapour carries it into the reaction tube 5 wherein a chemical reaction occurs with the deposition of a continuation layer containing the appropriate impurity. After the continuation layer has been deposited, the reaction tube is flushed with pure hydrogen and an opposite-type conductivity layer is then deposited on the continuation layer, substituting an opposite-type impurity in the liquid 25. Although not illustrated, a modified system may be provided in which the liquid 25 would contain N-type impurities and another container similar to container 20 having a liquid similar to liquid 25 with P-type impurities would be contained therein.

Many different semiconductor devices have been made by the epitaxial deposition method of the invention with different operable parameter variations, utilizing both germanium and silicon semiconductor materials. However in all cases during the epitaxial deposition of the continuation layer and the opposite-type conductivity layer, it is necessary to maintain the ratio of silicon halides to the impurity halides constant. However, some parameters such as the temperature to which the substrate is heated may be varied during the deposition.

In the specific examples hereinafter described, acceptable variations in processing

70

75

80

85

90

95

100

105

110

115

120

125

130

parameters for germanium and silicon will be apparent.

#### EXAMPLE I

A 0.01 ohm-cm. single crystal silicon substrate uniformly doped with antimony (about  $5 \times 10^{18}$  antimony atoms/cm<sup>3</sup>), is placed in the reaction furnace and heated to about 1250° C. The substrate is etched with hydrogen flowing at the rate of 10 litres per minute for about five to ten minutes. After the etching, silicon tetrachloride (SiCl<sub>4</sub>) doped with about 0.06 parts per million by volume of antimony pentachloride (SbCl<sub>5</sub>) is added to the hydrogen stream, the amount being metered at about 1.5 volume percent in the H<sub>2</sub> flow, the H<sub>2</sub> flow rate remaining the same. This effluent is passed over the heated substrate for about three minutes, the growth rate of the epitaxial deposit being about 0.1 mils per minute. Thus, a 0.3 mils thick N-type layer having a resistivity of 2 ohm-cm. is epitaxially deposited on the N+ (meaning heavily-doped) substrate. After the N-type continuation layer has been deposited on the silicon substrate, the reactor is flushed with H<sub>2</sub> for two to three minutes. Silicon tetrachloride doped with a hundred parts per million by volume of boron tribromide (BBr<sub>3</sub>) is then added to the hydrogen stream (flow rate remaining the same) by an amount of 1.5 percent by volume. This is passed over the substrate heated to about 1250° C., and a P-type layer having the resistivity of about 2 to 3 ohm-cm. is epitaxially deposited at the rate of about 0.1 mils per minute. The flow of this effluent is continued for only about 0.5 minutes; hence, a P-type conductivity layer is about 0.05 to 0.06 mils in thickness.

The device made by the above method was an N<sup>+</sup>N-P device having a breakdown voltage across the P-N junction of about 135 volts.

#### EXAMPLE II

A 0.001 ohm-cm. single crystal silicon substrate, uniformly doped with boron P+ (P+ being utilized to designate a highly doped substrate), is placed in the reaction tube and heated to about 1250° C. The substrate is etched with hydrogen flowing at a rate of 10 litres per minute for about five to ten minutes. After etching, silicon tetrachloride doped with a hundred parts per million of borontribromide was added to the hydrogen stream, the amount being metered to about 1.5 percent by volume in the hydrogen flow, the hydrogen flow rate remaining 10 liters per minute. This effluent was passed over the heated substrate for about three minutes, and the growth rate of the epitaxial deposit was sufficient to produce a 0.2 mils thick P-type layer thereon having a resistivity of 0.5 ohm-cm. (This continuation layer is designated P-type inasmuch as its resistivity is higher than the original P-type substrate). After forming the

P-type conductivity continuation layer, the reactor tube was flushed with pure hydrogen and an effluent containing silicon tetrachloride doped with 0.02 parts per million of antimony pentachloride was then flowed over the substrate. The flow of this effluent was continued for about ten minutes, during which a 1.1 mils thick N-type layer was deposited on the continuation layer, forming a P-N junction therebetween. The resistivity of the N-type layer was about 5.0 ohm-cm. A P-type impurity was then diffused by normal diffusion techniques into the N-type layer to form a transistor. After forming the P-type emitter region, the resulting effective thickness of the N-type layer between the P-type emitter and the P-type collector (the continuation layer) was about 0.3 mils. The transistor produced as above has a 300 volt base to collector breakdown voltage.

In the utilizing of the invention for silicon, of which the above two examples are illustrative, the minimum thickness of the continuation layer necessary to prevent contamination by diffusion or outgassing impurities from the substrate is 0.1 to 0.2 mils. For example, if a P-type layer of 2—3 ohm-cm. resistivity is to be epitaxially deposited on the continuation layer, an N-type continuation layer of approximately 0.2 mils thick will be required. However, if a P-type layer of about 0.5 ohm-cm. resistivity is to be epitaxially deposited on the continuation layer, the N-type continuation layer may be 0.1 mils thick.

Thus, it will be recognized that when the opposite-type conductivity layer is to be epitaxially deposited on the continuation layer, thinner continuation layers may be utilized for low resistivity opposite-type conductivity layers, whereas for higher resistivity opposite-type conductivity layers thicker continuation layers must be utilized. The reason for this is that the higher the impurity concentration in the opposite-type conductivity layer the lower the resistivity thereof. Thence, more opposite-type conductivity impurities require compensation by impurities diffusing from the substrate to raise the resistivity of the opposite-type conductivity layer.

For silicon, the parameters of the reaction illustrated in Figure 2 can be varied within the following limits:

1. Hydrogen flow rates for the unit can be varied between 1 and 20 litres per minute.
2. The volume of the silicon halide (with the impurity halide by volume remaining constant) in the hydrogen flow can vary between 0.1 and 6.0 volume percent.
3. The temperatures of substrate can be varied between 1150° C. and 1350° C.
4. All permutations of the above three parameters may be utilized.

Although the above parameters may be varied as described, caution should be exercised when a 1 inch diameter substrate is

provided. A differential temperature across the substrate in excess of 20° C. should be prevented.

Preferably arsenic or phosphorus-doped substrates should be avoided since these elements have high vapour pressures and high diffusion rates. Moreover, the preferable impurities for N-type silicon substrates are antimony and bismuth.

### EXAMPLE III

A germanium substrate doped N+ with antimony having a 0.015 ohm-cm. resistivity was placed in the reaction tube. The substrate was heated to about 850° C. and then hydrogen etched in a similar manner as in the silicon examples. The hydrogen flow rate was 3.5 litres per minute. A liquid of germanium tetrachloride containing 0.27 parts per million by volume of antimony pentachloride was injected into the hydrogen stream. The doped germanium tetrachloride flow was 2% by volume of the hydrogen stream. The above procedure epitaxially deposited a 0.5 ohm-cm. N-type continuation layer of germanium having a thickness of about 0.3 mils. The reactor tube was flushed with hydrogen and the temperature of the substrate was then raised to 880° C. Germanium tetrachloride doped with 0.4% by volume borontribromide was subsequently introduced at 0.6% by volume into the hydrogen flow, which was 11.2 litres per minute. Different temperatures for the N- and P-type layer deposition are used since in the deposition of the N-type layer, a temperature can be used whereby the diffusion of impurities from the substrate into the N-type layer is faster than the epitaxial growth of the N-type layer. This, of course, must be avoided to prevent contamination.

The P-type layer of germanium was 0.080 ohm-cm. having a thickness of 0.12 mils. This thickness of the P-type layer allows sufficient depth for an emitter region to be diffused therein. The minimum thickness of the continuation layer (N-type layer) that will allow a P-type layer to be epitaxially grown thereon without contamination is about 0.3 mils. The reaction parameters may be varied by all permutation within the following limits. The temperature of the substrate may be from about 800° C. to 880° C. The germanium tetrachloride concentration in the hydrogen stream may vary from 0.2% to 5.0% by volume whereas the H<sub>2</sub> flow may be varied from 2 litres per minute to 13 litres per minute.

It should be understood that an important feature of the invention is the formation of a continuation layer on the substrate of the same-type conductivity even though the resistivity of the layer is varied, and that after the continuation layer has been epitaxially grown on the substrate, additional epitaxial opposite-type conductivity layers may then be

deposited thereon. And although only one group of halide compounds has been utilized in describing the invention, it should be understood that many variations in the details of the process can be made without departing from the scope of the invention. For example, reactants which thermally decompose within the epitaxial temperature range could be utilized instead of reactants requiring hydrogen to promote decomposition. Moreover, although in epitaxial deposition techniques a flow process is more desirable, the advantages of the invention could be achieved in batch-type operations.

It should be understood that although the invention has been described with respect to silicon and germanium multi-layered devices, the features and advantages of the invention are readily adaptable to other epitaxial semiconductor processing techniques and such processes are within the scope of the invention.

### WHAT WE CLAIM IS:—

1. A method of forming P-N junctions in semiconductors by epitaxial deposition, comprising the steps of subjecting a semiconductor material substrate of one conductivity to a temperature suitable for promoting the epitaxial growth thereof, subjecting said semiconductor substrate at said temperature to a vapour containing a controlled ratio of a first volatilized compound of said semiconductor material and a second volatilized compound of a like-type conductivity-imparting impurity for a period of time to deposit epitaxially a like-type conductivity continuation layer of said semiconductor material on said substrate, and thereafter subjecting said substrate at said temperature to a second vapour containing a controlled ratio of said first volatilized compound and a third volatilized compound of an opposite-type conductivity-imparting impurity for a period of time to deposit epitaxially an opposite-type conductivity layer of said semiconductor material on said continuation layer.

2. A method according to claim 1 wherein said semiconductor material is silicon.

3. A method according to claim 1 or 2, wherein said substrate is of N-type conductivity silicon and wherein the layer deposited upon said continuation layer is of P-type silicon.

4. A method according to any one of the preceding claims wherein the substrate is silicon and is uniformly doped with antimony to about  $5 \times 10^{18}$  antimony atoms per cm<sup>3</sup> and said like-type conductivity-imparting impurity is antimony pentachloride.

5. A method according to any of claims 2, 3 and 4, wherein said opposite-type conductivity-imparting impurity is boron tribromide.

6. A method according to any one of the preceding claims in which the first mentioned



provided. A differential temperature across the substrate in excess of 20° C. should be prevented.

Preferably arsenic or phosphorus-doped substrates should be avoided since these elements have high vapour pressures and high diffusion rates. Moreover, the preferable impurities for N-type silicon substrates are antimony and bismuth.

### EXAMPLE III

A germanium substrate doped N+ with antimony having a 0.015 ohm-cm. resistivity was placed in the reaction tube. The substrate was heated to about 850° C. and then hydrogen etched in a similar manner as in the silicon examples. The hydrogen flow rate was 3.5 litres per minute. A liquid of germanium tetrachloride containing 0.27 parts per million by volume of antimony pentachloride was injected into the hydrogen stream. The doped germanium tetrachloride flow was 2% by volume of the hydrogen stream. The above procedure epitaxially deposited a 0.5 ohm-cm. N-type continuation layer of germanium having a thickness of about 0.3 mils. The reactor tube was flushed with hydrogen and the temperature of the substrate was then raised to 880° C. Germanium tetrachloride doped with 0.4% by volume borontribromide was subsequently introduced at 0.6% by volume into the hydrogen flow, which was 11.2 litres per minute. Different temperatures for the N- and P-type layer deposition are used since in the deposition of the N-type layer, a temperature can be used whereby the diffusion of impurities from the substrate into the N-type layer is faster than the epitaxial growth of the N-type layer. This, of course, must be avoided to prevent contamination.

The P-type layer of germanium was 0.080 ohm-cm. having a thickness of 0.12 mils. This thickness of the P-type layer allows sufficient depth for an emitter region to be diffused therein. The minimum thickness of the continuation layer (N-type layer) that will allow a P-type layer to be epitaxially grown thereon without contamination is about 0.3 mils. The reaction parameters may be varied by all permutation within the following limits. The temperature of the substrate may be from about 800° C. to 880° C. The germanium tetrachloride concentration in the hydrogen stream may vary from 0.2% to 5.0% by volume whereas the H<sub>2</sub> flow may be varied from 2 litres per minute to 13 litres per minute.

It should be understood that an important feature of the invention is the formation of a continuation layer on the substrate of the same-type conductivity even though the resistivity of the layer is varied, and that after the continuation layer has been epitaxially grown on the substrate, additional epitaxial opposite-type conductivity layers may then be

deposited thereon. And although only one group of halide compounds has been utilized in describing the invention, it should be understood that many variations in the details of the process can be made without departing from the scope of the invention. For example, reactants which thermally decompose within the epitaxial temperature range could be utilized instead of reactants requiring hydrogen to promote decomposition. Moreover, although in epitaxial deposition techniques a flow process is more desirable, the advantages of the invention could be achieved in batch-type operations.

It should be understood that although the invention has been described with respect to silicon and germanium multi-layered devices, the features and advantages of the invention are readily adaptable to other epitaxial semiconductor processing techniques and such processes are within the scope of the invention.

### WHAT WE CLAIM IS:—

1. A method of forming P-N junctions in semiconductors by epitaxial deposition, comprising the steps of subjecting a semiconductor material substrate of one conductivity to a temperature suitable for promoting the epitaxial growth thereof, subjecting said semiconductor substrate at said temperature to a vapour containing a controlled ratio of a first volatilized compound of said semiconductor material and a second volatilized compound of a like-type conductivity-imparting impurity for a period of time to deposit epitaxially a like-type conductivity continuation layer of said semiconductor material on said substrate, and thereafter subjecting said substrate at said temperature to a second vapour containing a controlled ratio of said first volatilized compound and a third volatilized compound of an opposite-type conductivity-imparting impurity for a period of time to deposit epitaxially an opposite-type conductivity layer of said semiconductor material on said continuation layer.

2. A method according to claim 1 wherein said semiconductor material is silicon.

3. A method according to claim 1 or 2, wherein said substrate is of N-type conductivity silicon and wherein the layer deposited upon said continuation layer is of P-type silicon.

4. A method according to any one of the preceding claims wherein the substrate is silicon and is uniformly doped with antimony to about  $5 \times 10^{18}$  antimony atoms per cm<sup>3</sup> and said like-type conductivity-imparting impurity is antimony pentachloride.

5. A method according to any of claims 2, 3 and 4, wherein said opposite-type conductivity-imparting impurity is boron tribromide.

6. A method according to any one of the preceding claims in which the first mentioned

controlled ratio and the second mentioned controlled ratio are retained constant during the respective vapour deposition periods.

- 5 7. A method according to any one of the preceding claims wherein said temperature suitable for promoting epitaxial growth is between 1150° C and 1350° C.

8. A method according to claim 1 wherein said semiconductor material is germanium.

- 10 9. A method according to claim 8, wherein said substrate is of N-type conductivity germanium and wherein the layer deposited upon said continuation layer is of P-type germanium.

- 15 10. A method according to claim 8 or 9, in which the first mentioned controlled ratio and the second mentioned controlled ratio are retained constant during the respective vapour deposition periods.

- 20 11. A method according to any of the preceding claims wherein hydrogen gas is em-

ployed as a carrier for conducting the controlled mixtures of the volatilized compounds to said semiconductor substrate and for conducting spent vapours away from said substrate. 25

12. A method of forming a P-N junction in a semiconductor by epitaxial deposition in accordance with any of Examples I, II, and III. 30

13. A P-N junction when formed in a semiconductor by epitaxial deposition by the method of any preceding claim.

H. D. FITZPATRICK & CO.,  
Chartered Patent Agents,  
3 Gray's Inn Square,  
London, W.C.1.  
and  
94 Hope Street,  
Glasgow, C.2.

Leamington Spa: Printed for Her Majesty's Stationery Office by the Courier Press.—1965.

Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.



\* C L M S \*