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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Method of providing Protection for a PN Junction Formed in a Silicon Body

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 providing protection for a PN junction formed in a silicon body to stabilize the electrical properties of silicon surfaces, and relates particularly to an improved method of cleaning and oxidising the surfaces of silicon diodes and other silicon semiconductor devices containing PN junctions. The characteristics of semiconductor devices are, in part, dependent upon conditions existing at their surfaces. In junction type devices, the protection of the exposed portion of the rectifying barrier is especially important.

Cleaning the surfaces of the device is very desirable because clean surfaces enhance the result obtained from oxidation of the surfaces. Oxidation alone, in fact, is relatively ineffective in producing stable surfaces unless they are cleaned before oxidation. For example, any organic material remaining on a surface at the time oxidation takes place tends to short the device and cause discontinuities in the oxide.

The use of steam as an oxidizing medium provides several advantages over free oxygen. When steam is used, no inversion layer is formed on the N side because of the absence of free oxygen. In steam, the oxide grows much faster than in free oxygen. Possibly, this occurs because of a difference in the oxidizing agent. Oxidation occurs at the silicon-silicon dioxide interface, and the oxidizing agent, possibly -OH ions, provided by the steam is able to penetrate the oxide faster than oxygen

can and thus reacts at a faster rate. After the steam oxidation, the silicon devices are cooled in an inert gas such as helium, thus avoiding free oxygen in the entire process.

An object of the present invention is to provide a method of providing protection for a PN junction formed in a silicon body. A further object of the present invention is to provide a silicon body containing a protected PN junction.

Another object is to provide a method of surface cleaning and oxidizing silicon diodes that will reduce the leakage current and only slightly reduce the breakdown voltage.

The present invention is a method of providing protection for a PN junction formed in a silicon body, comprising the steps of treating at least one surface of the silicon body with sulphuric acid, removing sulphate formed from the at least one surface, oxidizing the at least one surface in steam at about 1200°C and cooling the silicon body under inert gas.

The present invention is also a method of providing protection for a PN junction formed in a silicon body, comprising the steps of cleaning the surfaces of an etched silicon body with a series of solutions one of which is sulphuric acid, removing the sulphate formed from the surfaces of the body, oxidizing the surfaces in steam at atmospheric pressure for about five and one-half hours at 1200°C, drying the surfaces for one hour at 1200°C, and cooling the body in an inert gas for one hour.

The present invention is also a method of providing protection for a PN junction formed in a silicon body, which comprises the steps of degreasing a silicon body in trichloroethylene, rinsing it in methyl alcohol and water, boiling it for 20 minutes at 100°C in nitric acid, rinsing it in deionized water for 5 minutes, heating it in concentrated sulphuric acid at 200°C for 20 minutes and rinsing in deionized running water for 5 minutes, soaking it in hydrofluoric acid for 30 minutes and

5 rinsing in water for 5 minutes, boiling it in deionized water twice for 15 minutes and rinsing in water for 5 minutes, boiling it in nitric acid 30 minutes and rinsing in deionized running water for 30 minutes, oxidizing it about five and one-half hours in steam at atmospheric pressure at 1200°C, drying it in an inert gas for one hour and cooling it in the inert gas to room temperature.

10 A number of variations and advantages in the cleaning process may be devised, but the preferred process hereinafter described most advantageously utilizes the cleaning and surface treatment required in the pre-oxidation process.

15 The silicon diodes, comprised of mesa etched slices, are degreased in a soxhlet containing trichloroethylene, xylene or some other suitable solvent for thirty minutes.

20 The solvent is then removed by rinsing the slices in methyl alcohol and thereafter rinsing them in water. To ensure the complete removal of all organic material from the surface of each slice, the slices are subsequently boiled in nitric acid for twenty minutes at 100°C and afterwards rinsed in running deionized water for about five minutes. Surface treatment is finally accomplished by immersing the slices for about twenty minutes in concentrated sulphuric acid, heated to 200°C. Most of the sulphate which remains on the surface from the action of sulphuric acid is then removed by rinsing the slices for five minutes in running deionized water.

35 As above indicated, the water rinse does not completely remove all traces of the sulphate from the silicon wafer. Removal of the remainder is necessary as it contaminates the surface and increases the oxygen absorption at the surface. Moreover, oxygen, being a P-type dopant, will tend to cause an inversion layer at the surface of the wafer, while the oxygen and the sulphate degrade the reverse characteristics of a silicon diode. Oxygen, principally, seems to contribute to high

leakage while the sulphate tends to reduce the breakdown voltage. Results have shown that the use of a method which eliminates the presence of sulphate and free oxygen before and during oxidation and cooling of silicon diodes markedly reduces leakage and slightly reduces breakdown voltage.

The remaining sulphate is removed from the slices in the following manner: The slices are first soaked in hydrofluoric acid for thirty minutes. The acid that remains on the surfaces of the slices is then removed by rinsing the slices in water for about five minutes, then boiling them in deionized water twice for about fifteen minutes each, then rinsing them in water for about five minutes, then boiling them in nitric acid for about thirty minutes, and finally rinsing them in running deionized water for about thirty minutes.

The wet slices, now ready for oxidation, are placed in quartz boats, loaded into the oxidation furnace under steam and oxidized for about five and one-half hours at atmospheric pressure. When oxidation is completed steam is replaced by an inert gas such as helium, the slices are dried therein for about one hour at the oxidation temperature of 1200°C and then cooled to room temperature under helium for about one hour.

By the practice of this invention the tendency of silicon to absorb oxygen is reduced, and during the oxidation of the silicon with steam free oxygen is avoided. This results in minimizing the breakdown voltage degradation and lowering the leakage of the oxide protected junction. The oxide film coating the slice is approximately 20,000 Angstroms thick.

An example illustrating the improvement in leakage current and breakdown voltage by the practice of the invention is shown in Table I, in which results are compared when either oxygen or sulphate or both are allowed to come into contact with the slices, or remain on the slices during the operation of the method.

TABLE I

	Reverse Current at $V_z = 50V$		Breakdown Voltage	
	Before	After	Before	After
SO ₄ and O ₂	.25	.0090	375	50
SO ₄ only	1.20	.0033	275	110
O ₂ only	.29	2.4	360	275
SO ₄ and O ₂ both excluded	1.2	.0070	375	360

WHAT WE CLAIM IS:—

1. A method of providing protection for a PN junction formed in a silicon body,

comprising the steps of treating at least one surface of the silicon body with sulphuric acid, removing sulphate formed from the at



5 rinsing in water for 5 minutes, boiling it in deionized water twice for 15 minutes and rinsing in water for 5 minutes, boiling it in nitric acid 30 minutes and rinsing in deionized running water for 30 minutes, oxidizing it about five and one-half hours in steam at atmospheric pressure at 1200°C, drying it in an inert gas for one hour and cooling it in the inert gas to room temperature.

10 A number of variations and advantages in the cleaning process may be devised, but the preferred process hereinafter described most advantageously utilizes the cleaning and surface treatment required in the pre-oxidation process.

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25 boiled in nitric acid for twenty minutes at 100°C and afterwards rinsed in running deionized water for about five minutes. Surface treatment is finally accomplished by immersing the slices for about twenty minutes in concentrated sulphuric acid, heated to 200°C.

30 Most of the sulphate which remains on the surface from the action of sulphuric acid is then removed by rinsing the slices for five minutes in running deionized water.

35 As above indicated, the water rinse does not completely remove all traces of the sulphate from the silicon wafer. Removal of the remainder is necessary as it contaminates the surface and increases the oxygen absorption at the surface. Moreover, oxygen, being a P-type dopant, will tend to cause an inversion layer at the surface of the wafer, while the oxygen and the sulphate degrade the reverse characteristics of a silicon diode. Oxygen, principally, seems to contribute to high

leakage while the sulphate tends to reduce the breakdown voltage. Results have shown that the use of a method which eliminates the presence of sulphate and free oxygen before and during oxidation and cooling of silicon diodes markedly reduces leakage and slightly reduces breakdown voltage.

The remaining sulphate is removed from the slices in the following manner: The slices are first soaked in hydrofluoric acid for thirty minutes. The acid that remains on the surfaces of the slices is then removed by rinsing the slices in water for about five minutes, then boiling them in deionized water twice for about fifteen minutes each, then rinsing them in water for about five minutes, then boiling them in nitric acid for about thirty minutes, and finally rinsing them in running deionized water for about thirty minutes.

The wet slices, now ready for oxidation, are placed in quartz boats, loaded into the oxidation furnace under steam and oxidized for about five and one-half hours at atmospheric pressure. When oxidation is completed steam is replaced by an inert gas such as helium, the slices are dried therein for about one hour at the oxidation temperature of 1200°C and then cooled to room temperature under helium for about one hour.

By the practice of this invention the tendency of silicon to absorb oxygen is reduced, and during the oxidation of the silicon with steam free oxygen is avoided. This results in minimizing the breakdown voltage degradation and lowering the leakage of the oxide protected junction. The oxide film coating the slice is approximately 20,000 Angstroms thick.

An example illustrating the improvement in leakage current and breakdown voltage by the practice of the invention is shown in Table I, in which results are compared when either oxygen or sulphate or both are allowed to come into contact with the slices, or remain on the slices during the operation of the method.

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SO ₄ and O ₂ both excluded	1.2	.0070	375	360

WHAT WE CLAIM IS:—

1. A method of providing protection for a PN junction formed in a silicon body,

comprising the steps of treating at least one surface of the silicon body with sulphuric acid, removing sulphate formed from the at

least one surface, oxidizing the at least one surface in steam at about 1200°C, and cooling the silicon body under inert gas.

- 5 2. A method of providing protection for a PN junction formed in a silicon body, comprising the steps of cleaning the surfaces of an etched silicon body with a series of solutions one of which is sulphuric acid, removing the sulphate formed from the surfaces of the body, oxidizing the surfaces in steam at atmospheric pressure for about 10 five and one-half hours at 1200°C, drying the surfaces for one hour at 1200°C, and cooling the body in an inert gas for one hour.
- 15 3. A method as claimed in claim 2, wherein the inert gas is helium.
- 20 4. A method of providing protection for a PN junction formed in a silicon body which comprises the steps of degreasing a silicon body in trichloroethylene, rinsing it in methyl alcohol and water, boiling it for 20 minutes at 100°C in nitric acid, rinsing it in deionized water for 5 minutes, heating it in concentrated sulphuric acid at 200°C for 20 minutes and 25 rinsing in deionized running water for 5 minutes, soaking it in hydrofluoric acid for 30 minutes and rinsing in water for 5 minutes, boiling it in deionized water twice for 15 minutes and rinsing in water for 5 minutes, boiling it in nitric acid 30 minutes and rinsing in deionized running water for 30 minutes oxidizing it about five and one-half hours in steam at atmospheric pressure at 1200°C, drying it in an inert gas for one hour, and cooling it in the inert gas to room temperature. 30 35
5. A method as claimed in claim 4, wherein the inert gas is helium.
6. A method as claimed in claim 4 or 5, wherein an oxide layer having a thickness of approximately 20,000 Angstroms is formed. 40
7. A method of providing protection for a PN junction formed in a silicon body substantially as hereinbefore described.
8. A silicon body containing a PN junction which has been protected according to the method claimed in any of the preceding claims 45

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