

L055.724



PATENT SPECIFICATION

DRAWINGS ATTACHED

L055.724

Date of Application and filing Complete Specification: March 25, 1964.

No. 12712/64.

Application made in United States of America (No. 269,979) on April 2, 1963.

Complete Specification Published: Jan. 18, 1967.

© Crown Copyright 1967.

Index at acceptance:—H1 K(1A1, 1CX, 2S1B, 2S2P, 2S10, 2S20, 3E1M, 3J, 3T1, 4C21, 4C23, 4F1A, 5C5)

Int. Cl.:—H 0117/00

COMPLETE SPECIFICATION

Semiconductor Devices and method of making them

We, RADIO CORPORATION OF AMERICA, a Corporation organized under the laws of the State of Delaware, United States of America, of 30, Rockefeller Plaza, City and 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 more particularly to a method of fabricating them.

It is known to make semiconductor devices which include a surface layer of silicon oxide on at least a portion of the surface thereof. The surface layer of silicon oxide may be formed by an oxidizing bath or by anodic oxidation. When the semiconductor device is formed from a silicon wafer, the silicon oxide layer on the surface of the device may be formed by heating the wafer in an oxidizing atmosphere which includes water vapour. It has also been proposed to make transistors and other semiconductor devices by a process which includes forming a silicon oxide masking layer on a silicon wafer, removing portions of this layer to expose the wafer surface, diffusing conductivity type modifiers into the exposed portions, and making metallic contacts to the diffused areas. However, improvement is desirable in several respects, particularly with respect to improved operating life and improved resistance to elevated voltages.

Accordingly, it is an object of this invention to provide an improved method of fabricating semiconductor devices.

The method according to the present invention comprises the successive steps of: masking a portion of one major face of a semiconductor wafer of a given conductivity type with silicon oxide; diffusing conductivity modifiers into the unmasked portions of said wafer face; removing said silicon oxide mask; and cleaning

said one wafer face to remove contaminants therefrom.

The wafer surface is cleaned, for example by treatment with an acidified solution of hydrogen peroxide, to remove such residual contaminants as metal ions from parts of the wafer adjacent to the regions into which impurities have been deliberately introduced to control the conductivity type thereof.

The invention will be described with reference to the accompanying drawing, in which:

FIGURES 1—8 are cross-sectional views of a semiconductive wafer during successive steps in the fabrication of a semiconductor device according to one embodiment of the invention; and

FIGURE 9 is a flow sheet of the method of fabricating semiconductor devices according to this embodiment of the invention.

A semiconductive wafer 10 (FIGURE 1) of crystalline semi-conductive material is prepared with at least one major face 19. The semiconductor material may consist of silicon, silicon-germanium alloys, germanium, or the like. In this example, wafer 10 consists of monocrystalline silicon. The exact size and shape of semiconductive wafer 10 is not critical. In this example, wafer 10 is approximately 50 mils square and 5 mils thick. The semiconductive wafer may be of either conductivity type, or intrinsic, or compensated. In this example, wafer 10 is of N-type conductivity. A layer 11 of silicon oxide is now deposited on major wafer face 19 by any convenient method. When wafer 10 consists of materials other than silicon, such as germanium, gallium arsenide, or the like, the silicon oxide layer 11 may be deposited by thermally decomposing a siloxane compound, and passing the vaporized decomposition products of the compound over the surface of the wafer. When wafer 10 consists of silicon, as in this example, the silicon oxide layer 11 may be formed by heating wafer 10 in steam for approximately 30

[Price 4s. 6d.]

minutes at approximately 1100°C.

Referring now to FIGURE 2, one or more portions of the silicon oxide layer 11 are now removed by any convenient method, leaving in the layer 11 at least one aperture 12 in which is exposed a desired portion of wafer face 19. The desired portion of the silicon oxide layer 11 may be removed by either sand blasting or grinding. Alternatively, the silicon oxide layer 11 may be suitably masked with an acid resist (not shown) such as paraffin wax, or apiezon wax, or with a photoresist such as a bichromated protein, and the unmasked portions of silicon oxide layer 11 removed by means of a suitable etchant, such as a concentrated aqueous solution of hydrofluoric acid. A conductivity type modifier is then diffused into the unmasked portion of wafer face 19. If an acid resist or photoresist has been used to define the aperture 12, the resist is removed prior to the diffusion step. In this example, diffusion is accomplished by heating wafer 10 in a nitrogen ambient containing boron oxide vapours for approximately 35 minutes at 925°C, then heating the wafer in steam for approximately two hours at 1200°C. The boron diffuses into the unmasked portion of wafer face 19. Since boron is an acceptor in silicon, the boron-diffused wafer region 13 is converted to P-type conductivity, and a p-n junction 14 is formed at the interface between the P-type boron-diffused region 13 and the N-type bulk of wafer 10.

The unmasked portion of major face 19 is now covered with a mask 15 (FIGURE 3). The mask 15 may suitably consist of silicon oxide, and may be deposited by any convenient method, such as by thermally decomposing a siloxane compound to deposit silicon oxide on the wafer, as described above. Alternatively, when wafer 10 consists of silicon, as in this example, the silicon oxide layer 15 is formed during the diffusion step by the effect of steam on silicon.

Referring now to FIGURE 4, one or more portions of silicon oxide mask 15 are removed by any convenient method, leaving in the mask 15 at least one aperture 16 in which is exposed a desired portion of wafer face 19. A second diffusion is now accomplished by heating wafer 10 in an ambient containing a conductivity type modifier capable of inducing the original conductivity type of the wafer (N-type in this example). Conveniently, this is accomplished by heating wafer 10 in the vapours of phosphorus pentoxide for approximately 8 minutes at approximately 1100°C. The phosphorus, which is a donor in silicon diffuses into the unmasked portion of wafer face 19, and forms a phosphorus-diffused N-type region 17. The time, temperature and modifier concentration are selected so that region 17 is thinner than region 13, and is completely surrounded by region 13. A p-n junction 18 is formed at the interface between phosphorus-diffused N-type

region 17 and the boron-diffused P-type region 13.

All of the silicon oxide coating on wafer face 19 is now removed, leaving wafer 10 with its diffused surface exposed, as shown in FIGURE 5. The silicon oxide coating is conveniently removed by treating wafer 10 in a concentrated aqueous solution of hydrofluoric acid for a few minutes. The wafer is then washed in deionized or distilled water.

The surface of wafer 10 is now cleaned by treating the wafer in a bath having the composition 100 cc. concentrated hydrogen peroxide solution and 0.5 to 10 cc. of a concentrated strong acid, such as concentrated hydrochloric acid. In this example, the hydrogen peroxide solution contains approximately 30 weight percent H_2O_2 , and the bath contains 1 cc. concentrated hydrochloric acid per 100 cc. of the peroxide solution. The wafer is immersed in the bath at room temperature, and the bath is then heated to from 85° to 95°C. This treatment tends to remove any metallic traces or other impurities from the wafer surface, but the hydrogen peroxide may cause the formation of a thin silicon oxide surface film when the wafer consists of silicon, as in this example. The wafer is therefore treated again with concentrated hydrofluoric acid to remove any silicon oxide film that has been formed, then washed with boiling deionized or distilled water.

Referring now to FIGURE 6, a fresh layer or coating 21 of silicon oxide is now deposited on wafer face 19. The fresh silicon oxide coating 21 may be deposited by thermal oxidation of a siloxane compound, as described above. Since wafer 10 consists of silicon in this example, the fresh silicon oxide layer 21 is conveniently formed by heating wafer 10 in steam for approximately 15 minutes at 1100°C. During this heating step the phosphorus diffused region 17 becomes thicker.

Selected portions of silicon oxide coating 21 are now removed by any convenient method, such as grinding, sand blasting or etching. A ring-shaped portion 24 (FIGURE 7) of wafer face 19 within the P-type region 13 is thereby exposed, as well as a portion 22 of wafer face 19 within the N-type region 17.

Referring now to FIGURE 8, a metal such as aluminium is evaporated on the exposed portions of wafer face 19, thereby forming a metallic contact 25 to the N-type emitter region 17, and a contact 26 to the P-type base region 13. The device is subsequently completed by attaching electrical lead wires to contacts 25 and 26, mounting wafer 10 on a base plate, and casing the device. These steps are accomplished by techniques known to the art, and do not form a part of this invention.

It has unexpectedly been found that when semiconductor devices having a silicon oxide surface layer are fabricated as described above, with a silicon oxide layer utilized as a diffusion mask, then removed from the wafer and the

wafer surface treated to remove contaminants, the operating life of the device is improved. Moreover, the device thus fabricated shows improved resistance to elevated reverse voltages. While the exact mechanism responsible for the improvement is not understood, it is theorized that in devices made according to the prior art some traces of metallic and other impurities are present on the surface of the wafer and in the silicon oxide layer upon the wafer surface, and that these impurities migrate during the operation of the device, thereby adversely affecting the electrical parameters of the device. In the embodiment described above, the silicon oxide layer is removed, after all diffusion steps are complete, the exposed surface of the wafer is treated to remove metallic and other impurities, and a fresh clean layer of silicon oxide may then be deposited on the wafer. Accordingly, the amount of impurities present on the wafer surface and in the fresh silicon oxide layer is reduced, thereby improving the electrical parameters of the device, such as the breakdown voltage.

It will be understood that the above example is by way of illustration only, and not limitation, since various modifications and variations may be made without departing from the scope of the claimed invention. For example, only a single diffusion step may be utilized, and the devices may be made of semiconductive materials other than silicon. The hydrogen peroxide acid bath utilized may contain lesser amounts of hydrogen peroxide, and the wafer treated in the bath for longer periods of time. Other strong acids, such as hydrobromic acid and nitric acid, may be utilized instead of the hydrochloric acid.

WHAT WE CLAIM IS:—

1. A method of fabricating a semiconductor device, comprising the successive steps of: masking a portion of one major face of a semiconductive wafer of a given conductivity type with silicon oxide; diffusing conductivity modifiers into the unmasked portions of said wafer face; removing said silicon oxide mask; and cleaning said one wafer face to remove contaminants therefrom.

2. A method of fabricating a semiconductor device according to Claim 1 wherein the diffusion of conductivity modifiers into the wafer face is performed in the following manner: diffusing an opposite conductivity type modifier into the initially unmasked portions of said one wafer face to cause diffused regions to occur in said wafer, re-masking a portion of each of said diffused regions on said one wafer face; and diffusing a said given conductivity type modifier into the unmasked portions of said diffused regions.

3. A method of fabricating a semiconductor device according to Claim 1 or Claim 2, comprising the additional steps after the cleaning step, of: forming a fresh silicon oxide layer upon said major wafer face; removing portions

of said fresh silicon oxide layer; and, depositing metallic contacts on the exposed portions of said major wafer face.

4. A method of fabricating a semiconductor device according to Claim 1 or Claim 2 comprising the additional step after the cleaning step of: forming a fresh silicon oxide layer upon said major wafer face.

5. A method of fabricating a semiconductor device according to Claim 2 which comprises using an acidified hydrogen peroxide solution in the cleaning step to remove contaminants from said one wafer face; and, then forming a fresh silicon oxide layer upon said one wafer face.

6. A method of fabricating a semiconductor device according to Claim 1 which comprises cleaning said one wafer face by treating said wafer with a mixture of hydrogen peroxide and a strong acid; and then forming a fresh silicon oxide layer upon said major face.

7. A method of fabricating a semiconductor device according to Claim 1 or Claim 2 in which the cleaning step comprises treating said wafer with a mixture of hydrogen peroxide and hydrochloric acid; and then treating said wafer with hydrofluoric acid; and in which, after the cleaning step a silicon oxide layer is re-formed on the wafer.

8. A method of fabricating a semiconductor device according to Claim 1 or Claim 2 in which the cleaning step comprises treating said wafer with a mixture of hydrogen peroxide and hydrochloric acid; treating said wafer with hydrofluoric acid; and then washing said wafer with water; and in which a silicon oxide layer is re-formed on the wafer after the cleaning step.

9. A method of fabricating a semiconductor device according to Claim 1 or Claim 2 which comprises: treating said wafer with hydrofluoric acid to remove said silicon oxide mask; and cleaning by first treating said wafer with a mixture of hydrogen peroxide and hydrochloric acid; and by then treating said wafer with hydrofluoric acid; and finally washing said wafer with water; and re-forming a silicon oxide layer thereupon.

10. A method of fabricating a semiconductor device according to any one of the preceding claims, in which the or each silicon oxide layer is formed on said wafer by heating said wafer in steam.

11. A method of fabricating a semiconductor device according to any one of Claims 1 to 3 which comprises: cleaning said one wafer face by first treating said wafer with a mixture consisting of 100 volumes concentrated hydrogen peroxide and one-half to ten volumes of concentrated hydrochloric acid; by then treating said wafer with hydrofluoric acid; and finally by washing said wafer with water; and then forming a silicon oxide layer on said wafer by heating said wafer in steam.

12. A method of fabricating a semiconductor



wafer surface treated to remove contaminants, the operating life of the device is improved. Moreover, the device thus fabricated shows improved resistance to elevated reverse voltages. While the exact mechanism responsible for the improvement is not understood, it is theorized that in devices made according to the prior art some traces of metallic and other impurities are present on the surface of the wafer and in the silicon oxide layer upon the wafer surface, and that these impurities migrate during the operation of the device, thereby adversely affecting the electrical parameters of the device. In the embodiment described above, the silicon oxide layer is removed, after all diffusion steps are complete, the exposed surface of the wafer is treated to remove metallic and other impurities, and a fresh clean layer of silicon oxide may then be deposited on the wafer. Accordingly, the amount of impurities present on the wafer surface and in the fresh silicon oxide layer is reduced, thereby improving the electrical parameters of the device, such as the breakdown voltage.

It will be understood that the above example is by way of illustration only, and not limitation, since various modifications and variations may be made without departing from the scope of the claimed invention. For example, only a single diffusion step may be utilized, and the devices may be made of semiconductive materials other than silicon. The hydrogen peroxide acid bath utilized may contain lesser amounts of hydrogen peroxide, and the wafer treated in the bath for longer periods of time. Other strong acids, such as hydrobromic acid and nitric acid, may be utilized instead of the hydrochloric acid.

WHAT WE CLAIM IS:—

1. A method of fabricating a semiconductor device, comprising the successive steps of: masking a portion of one major face of a semiconductive wafer of a given conductivity type with silicon oxide; diffusing conductivity modifiers into the unmasked portions of said wafer face; removing said silicon oxide mask; and cleaning said one wafer face to remove contaminants therefrom.
2. A method of fabricating a semiconductor device according to Claim 1 wherein the diffusion of conductivity modifiers into the wafer face is performed in the following manner: diffusing an opposite conductivity type modifier into the initially unmasked portions of said one wafer face to cause diffused regions to occur in said wafer, re-masking a portion of each of said diffused regions on said one wafer face; and diffusing a said given conductivity type modifier into the unmasked portions of said diffused regions.
3. A method of fabricating a semiconductor device according to Claim 1 or Claim 2, comprising the additional steps after the cleaning step, of: forming a fresh silicon oxide layer upon said major wafer face; removing portions

of said fresh silicon oxide layer; and, depositing metallic contacts on the exposed portions of said major wafer face.

4. A method of fabricating a semiconductor device according to Claim 1 or Claim 2 comprising the additional step after the cleaning step of: forming a fresh silicon oxide layer upon said major wafer face.

5. A method of fabricating a semiconductor device according to Claim 2 which comprises using an acidified hydrogen peroxide solution in the cleaning step to remove contaminants from said one wafer face; and, then forming a fresh silicon oxide layer upon said one wafer face.

6. A method of fabricating a semiconductor device according to Claim 1 which comprises cleaning said one wafer face by treating said wafer with a mixture of hydrogen peroxide and a strong acid; and then forming a fresh silicon oxide layer upon said major face.

7. A method of fabricating a semiconductor device according to Claim 1 or Claim 2 in which the cleaning step comprises treating said wafer with a mixture of hydrogen peroxide and hydrochloric acid; and then treating said wafer with hydrofluoric acid; and in which, after the cleaning step a silicon oxide layer is re-formed on the wafer.

8. A method of fabricating a semiconductor device according to Claim 1 or Claim 2 in which the cleaning step comprises treating said wafer with a mixture of hydrogen peroxide and hydrochloric acid; treating said wafer with hydrofluoric acid; and then washing said wafer with water; and in which a silicon oxide layer is re-formed on the wafer after the cleaning step.

9. A method of fabricating a semiconductor device according to Claim 1 or Claim 2 which comprises: treating said wafer with hydrofluoric acid to remove said silicon oxide mask; and cleaning by first treating said wafer with a mixture of hydrogen peroxide and hydrochloric acid; and by then treating said wafer with hydrofluoric acid; and finally washing said wafer with water; and re-forming a silicon oxide layer thereupon.

10. A method of fabricating a semiconductor device according to any one of the preceding claims, in which the or each silicon oxide layer is formed on said wafer by heating said wafer in steam.

11. A method of fabricating a semiconductor device according to any one of Claims 1 to 3 which comprises: cleaning said one wafer face by first treating said wafer with a mixture consisting of 100 volumes concentrated hydrogen peroxide and one-half to ten volumes of concentrated hydrochloric acid; by then treating said wafer with hydrofluoric acid; and finally by washing said wafer with water; and then forming a silicon oxide layer on said wafer by heating said wafer in steam.

12. A method of fabricating a semiconductor

- device according to any one of the preceding claims which comprises, treating said wafer with hydrofluoric acid to remove said silicon oxide mask; washing said wafer with deionized water; treating said wafer with a mixture consisting of 100 volumes concentrated hydrogen peroxide and one volume of concentrated hydrofluoric acid; treating said wafer with concentrated hydrofluoric acid; washing said wafer with boiling deionized water; and then forming a silicon oxide layer on said wafer by heating said wafer in steam.

13. A method of fabricating a semiconductor device substantially as hereinbefore described with reference to the accompanying drawings.

14. A semiconductor device when fabricated by a method according to any one of the preceding claims.

A. M. & WM. CLARK,
Chartered Patent Agents,
5 Stone Buildings,
Chancery Lane,
London, W.C.2.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press (Leamington) Ltd.—1967. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.

