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PATENT SPECIFICATION 1,061,629

DRAWINGS ATTACHED.

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COMPLETE SPECIFICATION.

Semiconductor Device Fabrication.

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 a method of fabricating semiconductor devices, particularly, though not exclusively, multijunction semiconductor devices.

It is desired to prepare triple-layer double-junction semiconductor wafers which are unsymmetrical in that the converted layers adjacent to opposite major wafer faces differ in respect to thickness or surface conductivity (surface impurity concentration), and doping gradient (or conductivity gradient).

This object is attained according to the present invention by a method which comprises the steps of depositing on opposing major faces of a semiconductive wafer coatings comprising silicon oxide and containing a conductivity modifier, the concentration of said modifier being higher in the coating on one said face than in that coating on the other said face, and then simultaneously diffusing the modifier from each of the coatings into the wafer so as to provide simultaneously a higher concentration of conductivity modifiers on one face than on the other face.

By "concentration", with respect to the conductivity modifiers, we mean total amount per unit area of surface.

According to one embodiment of the present invention, the higher concentration of the conductivity modifier in the coating on one face of the wafer is obtained by a deposition step wherein the conductivity modifier is deposited on this face only. During an additional deposition step in this process, both sides are provided with similar amounts of conductivity modifier. Therefore, one face receives conductivity modifier from both deposition steps, whereas the other face receives it only in one step. Thus there is provided a higher concentration of conductivity modifier on one face than on the other face.

In another embodiment of the present invention, a coating is deposited on one face only with a given amount of conductivity modifier therein. Then a coating is deposited on the other face with an amount of conductivity modifier different from (higher or lower) than the amount deposited on the other face during the first deposition. Thus the desired difference in concentration of conductivity modifier is provided.

The invention will be described in greater detail with reference to the accompanying drawings, in which:

Figure 1 is a cross-sectional schematic view of one form of apparatus useful in carrying out the method of the invention;

Figure 2 is a cross-sectional schematic view of another form of apparatus;

Figures 3—11 are cross-sectional views of a semiconductor wafer during successive steps in an embodiment of the method of the invention.

The apparatus 10 (Figure 1) comprises a refractory furnace tube 11 which may, for example, consist of a high melting glass, or of fused silica. Furnace tube 11 has at one end a stopper 12 containing an inlet tube 13, and at the other end a stopper 14 containing an outlet tube 15. Around a central portion of furnace tube 11 is a furnace 16, which is, for example, an electrical resistance furnace. Advantageously, the temperature of furnace

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16 is kept within the desired temperature range by means of a controller 17, which is connected by a pair of electrical lead wires 18 to the furnace 16. Furnace tube 11 contains a quartz temperature sensing element 19 which is mounted in outlet stopper 14. The temperature sensing element 19 contains a temperature sensing device such as a thermocouple (not shown) which is connected by a pair of electrical lead wires 20 to the controller 17. A holder 21 is supported by the temperature sensing element 19. The semiconductor wafer 30 to be treated is placed on the holder 21. A gas bubbler 23 feeds into the inlet tube 13. The bubbler 23 contains a liquid 24 consisting of a silicon compound which will decompose upon heating to silicon oxide, such as an organic siloxane compound. Dissolved therein is a substance that modifies the conductivity type of the particular semiconductor being processed, that is, a substance which contains a suitable doping agent for the particular semiconductor. Inlet tube 13 also includes stopcocks 25 and 26 in the entrance and exit respectively of bubbler 23. The bubbler 23 may thus be by-passed when desired by means of stopcocks 25 and 26. Ahead of the bubbler 23 in the gas train is a gas dryer 27 and a flowmeter 28 for controlling the flow of the inert carrier gas which is introduced into the bubbler 23 from a gas source (not shown), which maybe a tank or a line. The outlet tube 15 leads to a gas scrubber 29. The carrier gas is passed through the apparatus 10 in the direction indicated by the arrows, and leaves scrubber 29 by way of the exhaust. Suitably, the inlet tube 13 the outlet tube 15, the holder 21 and the scrubber 29 are all made of a refractory material such as fused quartz.

EXAMPLE 1

Referring now to Figure 3, a slice or wafer 30 of crystalline semiconductive material is prepared with two opposing major faces 31 and 32. The exact dimensions and conductivity of wafer 30 are not critical. In this example, wafer 30 is a slice of an N-type monocrystalline silicon ingot, is about 10 mils thick, and has a resistivity of 20—40 ohm—cm.

An acceptor-doped silicon oxide coating is deposited on semiconductive wafer 30, using the apparatus described above, as follows. The semiconductive wafer 30, which in this example consists of N-type silicon, is etched, cleaned, dried, then positioned on holder 21 and introduced into furnace tube 11. Furnace tube 11 is stoppered and suitably positioned in furnace 16. In this Example, the furnace control 17 is set to maintain the temperature inside furnace tube 11 at approximately 730°C. Most organic siloxane compounds begin to decompose at approximately 600°C. The inert carrier gas utilized may, for example, be nitrogen, argon, or helium. Hydrogen and hydrogen-nitrogen mixtures known as forming gas may also be utilized as the carrier gas. In this Example, the carrier gas consists of argon, the liquid siloxane compound 24 in bubbler 23 consists of ethyl silicate, and the substance containing the conductivity type modifier or doping agent dissolved therein consists of trimethylborate. The proportions of the siloxane compound and the substance containing the conductivity modifier may be varied to obtain different concentrations of the doping agent or active impurity in the silicon oxide layers deposited. In this example, the liquid 24 inside bubbler 23 consists of 10 millilitres ethyl silicate and 1 millilitre trimethylborate.

Line argon is passed through the system at the rate of approximately two cubic feet per hour while the furnace 16 is warmed to the desired temperature. During this period, the bubbler 23 is bypassed. When the temperature inside furnace tube 11 has reached 730°C, the flow of argon is switched by means of stopcocks 25 and 26 so as to bubble through the doped siloxane liquid 24. The mixed vapours of ethyl silicate and trimethylborate are swept by the argon through the inlet tube 13 into the furnace tube 11, where they are decomposed. A layer or coating of boron-containing silicon oxide 33 (Figure 4) is thus deposited on major face 31 of wafer 30, and a similar silicon oxide coating 34 (Figure 4) is deposited on major face 32. The carrier gas and the remaining decomposition products leave the system by way of the exhaust. After 10 to 20 minutes of deposition of the boron-doped silicon oxide layers, the flow of the carrier gas is switched back by means of stopcocks 25 and 26, that is, the bubbler 23 is again bypassed, and the furnace 16 is shut off. When the temperature inside the furnace tube 11 drops to approximately 200°C, the flow of the carrier gas may be turned off completely, and the wafer 30 removed from the furnace tube 11.

The concentration of boron in only ~~one~~ one of the silicon oxide layers 33 and 34 then is increased. To accomplish this, the surface of silicon oxide layer 33 is painted with a solution of a boron compound, such as boric acid, dissolved in a suitable solvent, such as "Cellosolve" (Registered Trade Mark). A film 35 containing additional boron thus is formed at the surface of the silicon oxide layer 33 previously doped with boron.

The wafer 30 is now heated at approximately 1300°C for approximately 14 hours so as to diffuse boron from the two silicon oxide coatings 33 and 34 into the adjacent portions of wafer 30. A wafer region 38

(Figure 6) adjacent to wafer face 32 is thus converted to P conductivity type, and a P—N junction 39 is formed between the P type region 38 and the N type bulk of wafer 30. At the same time, a wafer region 36 (Figure 6) adjacent to wafer face 31 is converted to P+ conductivity, and a P—N junction 37 is formed between the P type wafer region 36 and the N type bulk of wafer 30. The two boron-diffused wafer regions 36 and 38 are unsymmetrical. Wafer region 36 is more heavily doped than wafer region 38, has a higher surface concentration of boron, and a steeper conductivity gradient, because the boron diffusion source on face 31 of the wafer was made more concentrated by the presence of film 35 than the boron diffusion source on face 32 of the wafer. In this Example, wafer region 36 is approximately 2.5 mils thick, and has a surface concentration of approximately 10^{21} boron atoms per cm^3, while wafer region 38 is approximately 1.8 mils thick and has a surface concentration of approximately 2×10^{18} boron atoms per cm^3. The steepness of the conductivity gradient in region 36 is shown by the decline in boron atom concentration in region 36 from 10^{21} atoms per cm^3 at the surface to approximately 10^{14} atoms per cm^3 at the junction 37.

Now the silicon oxide layers 33 and 34, together with what remains of boron oxide layer 35, are removed by etching the wafer in hydrofluoric acid, leaving the wafer as shown in Figure 7, with a P+NP structure.

EXAMPLE II

In a similar manner to Example I, the excess concentration of conductivity modifier may be painted on one face only prior to deposition of coatings on both faces containing substantially equal concentrations of conductivity modifier. In this Example the wafer is of P type, and the conductivity modifier is N type, e.g. phosphorus formed from P_2O_5 in "Cellosolve". Thus an N+PN structure is produced.

EXAMPLE III

Alternatively to Example I, an organic siloxane compound may be thermally decomposed, and the decomposition products of the compound forced through a jet so as to impinge upon and coat a semiconductive body with silicon oxide. A special utility of this method is that it requires only moderate heating of the semiconductive body. The apparatus 10^1 shown in Figure 2 comprises a flow meter 28 for regulating the flow of the carrier gas, a drying column 27 for purification of the carrier gas, and an inlet tube 13 provided with stopcocks 25 and 26 for bypassing a bubbler 23^1. The bubbler 23^1 of this Example is somewhat different in form from that described above in connection with Figure I, but contains a similar liquid mixture 24 consisting of an organic siloxane compound together with a substance containing a doping agent, and functions in a similar manner. The organic siloxane compound, for example, consists of ethyl triethoxysilane. Inlet tube 13 is attached to one end of furnace tube 11. The tube 11 is surrounded by furnace 16, which is maintained at approximately 700°C. Since siloxane compounds generally begin to decompose at approximately 600°C, the furnace temperature of 700°C is sufficient to ensure pyrolysis of siloxane vapours introduced into the furnace. The mixed vapours of the inert carrier gas, the doping agent, and the thermal decomposition products of the siloxane compound exit from the other end of furnace tube 11 by way of a jet 32, and the jet stream (not shown) thus formed impinges upon the semiconductive wafer 30. The jet stream cools off rapidly as it leaves the jet 32, and hence the temperature of the jet stream at the point where it impinges on the semiconductive wafer 30 may be varied by adjusting the distance between the jet or orifice 32 and the wafer 30. For a furnace temperature of approximately 700°C, and a separation between jet 32 and wafer 30 of approximately 2 millimetres, the temperature of the jet impinging upon the wafer is approximately 150°C. Doped silicon oxide coatings can be deposited by this technique on semiconductive wafers while maintaining the wafer at very moderate temperatures. This technique is particularly useful with low energy gap semiconductors, which cannot withstand high temperatures.

A wafer of given conductivity type crystalline semiconductive material is prepared with two opposing major faces. A silicon oxide layer containing an opposite conductivity type modifier is deposited on one major wafer face only by positioning the wafer face to face with the jet. The amount of doping agent in the liquid mixture is then increased, for example, by doubling the ratio of the substance containing the conductivity modifier to siloxane compound in the mixture, and the other wafer face is positioned to face the jet. A doped silicon oxide layer is then deposited on this wafer face 31 only; the concentration of the doping agent in this layer is greater therefore than the concentration of the same doping agent in silicon oxide layer 34. The wafer is then heated for a time and temperature sufficient to diffuse some of the doping agent from the silicon oxide layers into the bulk of the wafer. The remaining steps are the same as in the previous Examples.

WHAT WE CLAIM IS:—

1. A method of fabricating a semiconductor device comprising the steps of de-

(Figure 6) adjacent to wafer face 32 is thus converted to P conductivity type, and a P—N junction 39 is formed between the P type region 38 and the N type bulk of wafer 30. At the same time, a wafer region 36 (Figure 6) adjacent to wafer face 31 is converted to P+ conductivity, and a P—N junction 37 is formed between the P type wafer region 36 and the N type bulk of wafer 30. The two boron-diffused wafer regions 36 and 38 are unsymmetrical. Wafer region 36 is more heavily doped than wafer region 38, has a higher surface concentration of boron, and a steeper conductivity gradient, because the boron diffusion source on face 31 of the wafer was made more concentrated by the presence of film 35 than the boron diffusion source on face 32 of the wafer. In this Example, wafer region 36 is approximately 2.5 mils thick, and has a surface concentration of approximately 10^{21} boron atoms per cm^3, while wafer region 38 is approximately 1.8 mils thick and has a surface concentration of approximately 2×10^{18} boron atoms per cm^3. The steepness of the conductivity gradient in region 36 is shown by the decline in boron atom concentration in region 36 from 10^{21} atoms per cm^3 at the surface to approximately 10^{14} atoms per cm^3 at the junction 37.

Now the silicon oxide layers 33 and 34, together with what remains of boron oxide layer 35, are removed by etching the wafer in hydrofluoric acid, leaving the wafer as shown in Figure 7, with a P+NP structure.

Example II

In a similar manner to Example I, the excess concentration of conductivity modifier may be painted on one face only prior to deposition of coatings on both faces containing substantially equal concentrations of conductivity modifier. In this Example the wafer is of P type, and the conductivity modifier is N type, e.g. phosphorus formed from P_2O_5 in "Cellosolve". Thus an N+PN structure is produced.

Example III

Alternatively to Example I, an organic siloxane compound may be thermally decomposed, and the decomposition products of the compound forced through a jet so as to impinge upon and coat a semiconductive body with silicon oxide. A special utility of this method is that it requires only moderate heating of the semiconductive body. The apparatus 10^1 shown in Figure 2 comprises a flow meter 28 for regulating the flow of the carrier gas, a drying column 27 for purification of the carrier gas, and an inlet tube 13 provided with stopcocks 25 and 26 for bypassing a bubbler 23^1. The bubbler 23^1 of this Example is somewhat different in form from that described above in connection with Figure I, but contains a similar liquid mixture 24 consisting of an organic siloxane compound together with a substance containing a doping agent, and functions in a similar manner. The organic siloxane compound, for example, consists of ethyl triethoxysilane. Inlet tube 13 is attached to one end of furnace tube 11. The tube 11 is surrounded by furnace 16, which is maintained at approximately 700°C. Since siloxane compounds generally begin to decompose at approximately 600°C, the furnace temperature of 700°C is sufficient to ensure pyrolysis of siloxane vapours introduced into the furnace. The mixed vapours of the inert carrier gas, the doping agent, and the thermal decomposition products of the siloxane compound exit from the other end of furnace tube 11 by way of a jet 32, and the jet stream (not shown) thus formed impinges upon the semiconductive wafer 30. The jet stream cools off rapidly as it leaves the jet 32, and hence the temperature of the jet stream at the point where it impinges on the semiconductive wafer 30 may be varied by adjusting the distance between the jet or orifice 32 and the wafer 30. For a furnace temperature of approximately 700°C, and a separation between jet 32 and wafer 30 of approximately 2 millimetres, the temperature of the jet impinging upon the wafer is approximately 150°C. Doped silicon oxide coatings can be deposited by this technique on semiconductive wafers while maintaining the wafer at very moderate temperatures. This technique is particularly useful with low energy gap semiconductors, which cannot withstand high temperatures.

A wafer of given conductivity type crystalline semiconductive material is prepared with two opposing major faces. A silicon oxide layer containing an opposite conductivity type modifier is deposited on one major wafer face only by positioning the wafer face to face with the jet. The amount of doping agent in the liquid mixture is then increased, for example, by doubling the ratio of the substance containing the conductivity modifier to siloxane compound in the mixture, and the other wafer face is positioned to face the jet. A doped silicon oxide layer is then deposited on this wafer face 31 only; the concentration of the doping agent in this layer is greater therefore than the concentration of the same doping agent in silicon oxide layer 34. The wafer is then heated for a time and temperature sufficient to diffuse some of the doping agent from the silicon oxide layers into the bulk of the wafer. The remaining steps are the same as in the previous Examples.

WHAT WE CLAIM IS:—

1. A method of fabricating a semiconductor device comprising the steps of de-

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positing on opposite major faces of a semiconductor wafer coatings comprising silicon oxide and containing a conductivity modifier, the concentration of said modifier being higher in the coating on one said face than in that on the other said face, and then simultaneously diffusing said modifier from each of said coatings into said wafer so as to provide simultaneously a higher concentration of conductivity modifiers on one face than on the other face.

2. A method according to Claim 1, wherein said semiconductive wafer is of a given conductivity type and said conductivity modifier is of an opposite type.

3. A method according to Claim 1 or Claim 2, wherein substantially equal concentrations of conductivity modifier are first deposited on said faces, and in a separate step prior to heating the concentration of said conductivity modifier in one of said coatings only is increased relative to the other.

4. A method according to Claim 1 or Claim 2, wherein said higher concentration of conductivity modifier in the coating on one of said faces is produced by depositing a coating having a given concentration of conductivity modifier on one face only and in a separate step, depositing a coating on the other face having a higher concentration of conductivity modifier than that on said one face.

5. A method according to Claim 1 or Claim 2, wherein a coating containing a given concentration of conductivity modifier is deposited on one face only, and then deposition is carried out on both faces with substantially equal concentrations of conductivity modifier, thereby to provide a different concentration of conductivity modifier on said faces.

6. A method of fabricating a semiconductor device substantially as hereinbefore described with reference to Figures 3—11 of the accompanying drawings.

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

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