

PATENT SPECIFICATION

DRAWINGS ATTACHED

1,055,837

Date of Application and filing Complete Specification: June 26, 1964.

No. 26601/64.

Application made in United States of America (No. 295,883) on July 18, 1963.

Complete Specification Published: Jan. 18, 1967.

© Crown Copyright 1967.



Index at acceptance:—C7 F (1B5, 2K, 2Z4, 2Z6, 4W, 4X, 5A)

Int. Cl.:—C 23 c 11/00

COMPLETE SPECIFICATION

Improved methods of manufacturing Semiconductor Devices

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 methods of manufacturing semiconductor devices, and concerns particularly, the fabrication of epitaxial germanium layers on semiconductive wafers.

Epitaxial layers are surface layers deposited on a substrate under such conditions that the crystal structure of the deposited layer is influenced by the nature of the substrate surface, so that a highly oriented surface layer is obtained whose crystallographic orientation is determined by the crystal structure of the substrate. The epitaxial layer may consist of the same material as the substrate, or may consist of a different but compatible material. Epitaxial layers on semiconductive wafers have become increasingly important in semiconductor device fabrication, since they enable the fabrication of semiconductor devices having regions of controlled thickness and resistivity.

Epitaxial layers on semiconductive wafers have been fabricated by forming a halogen compound of a semiconductor such as germanium, silicon, and like compound, then passing the vapours of the halogen compound over a heated wafer of the particular semiconductor, and reducing the halogen compound with hydrogen. Although epitaxial layers can be fabricated in this manner, the vaporized halides tend to attack the substrates, and also to transport conductivity modifiers, so that the junctions between the substrate wafer are not as abrupt, and the resistivity of the epitaxial layer is not as high or as uniform, as is desirable for some device applications.

Attempts have been made to deposit epitax-

ial germanium layers on a semiconductive wafer by heating the wafer in an ambient of germane (GeH_4) to a temperature high enough to decompose the germane. However, epitaxial layers deposited in this way have not proved entirely satisfactory.

According to the present invention, there is provided a method of manufacturing a semiconductor device comprising the steps of: heating a semiconductor wafer in a reaction vessel in the presence of hydrogen; and passing a mixture of germane and hydrogen over the heated surface of the wafer so as to decompose said germane and deposit on said wafer surface as an epitaxial germanium layer.

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

FIGURE 1 is a flow sheet of a method of depositing an epitaxial germanium layer on a semiconductive wafer according to one embodiment of the invention;

FIGURE 2 is a schematic cross sectional view of apparatus useful in carrying out the methods of this invention;

FIGURES 3a—3c are cross sectional views of a wafer during successive steps in one method of manufacturing a semiconductor device according to the invention; and,

FIGURES 4a—4b are cross sectional views of a wafer during successive steps in the manufacture of a semiconductor device according to another embodiment.

Apparatus 10 (Figure 2) for carrying out the methods of this invention comprises a deposition chamber or reaction vessel 11 surrounded by an RF coil 12. The reaction vessel 11 includes a susceptor block 13 mounted on a support 14; an inlet tube 15, and an outlet tube 16. The reaction chamber 11 and its associated tubing are preferably made of a refractory insulating material such as fused quartz. The susceptor block 13 is used to provide sufficient coupling with the RF coil 12, since the mass of the substrate wafer 31 is small.

[Price 4s. 6d.]

In this example, susceptor block 13 consists of a high conductivity germanium. The volume of apparatus 10 is approximately two litres.

Feeding into inlet tube 15 are three gas sources: a cylinder 17 of HCl gas; a palladium diffused hydrogen source 19; and a cylinder 21 of germane. The flow from the three gas sources 17, 19 and 21 is controlled by valves 18, 20 and 22 respectively. Advantageously, flow meters (not shown) may be utilized to monitor the rate of flow of each gas.

Outlet tube 16 is connected to tubes 23 and 24. Tube 23 carries a pressure gauge 25 and includes a valve 26 connected by a cold trap 30 to a mechanical vacuum pump. Tube 24 includes a valve 27, which can selectively connect tube 24 to either a hydrogen burner 28, or through a cold trap 29 to a hydrogen chloride fore pump.

Some Examples of the method according to this invention will now be described:

EXAMPLE I

A wafer 31 (FIGURE 3a) of monocrystalline semiconductive material is prepared with two opposing major faces 33 and 35. The major wafer faces 33 and 35 are preferably normal to the (111) crystal axis of the wafer. The exact size, shape and resistivity of wafer 31 is not critical. In this Example, wafer 31 is approximately 50 mils square, 5 mils thick, and consists of N-type germanium heavily doped so as to exhibit an electrical resistivity of approximately 0.001 ohm-cm.

The germanium wafer 31 is positioned on susceptor block 13 in apparatus 10 while all the valves are closed. Valve 26 is then opened, and reaction vessel 11 evacuated through cold trap 30 by means of the mechanical vacuum pump until the ambient pressure in vessel 11 is reduced below 0.1 microns Hg. Valve 20 is then opened and the reaction vessel 11 is flushed with pure dry palladium diffused hydrogen. The flow of hydrogen is monitored at approximately ten litres per minute and passes by way of outlet tube 16 and valve 27 to the hydrogen burner 28.

While continuing the flow of hydrogen, electrical power is supplied to the RF coil 12 so as to heat susceptor block 13 and germanium wafer 31 to a temperature of approximately 900°C. Valve 18 is then opened, and a mixture of approximately eleven volumes HCl gas and two volumes hydrogen are permitted to flow through the reaction vessel 11 for approximately ten minutes while maintaining wafer 31 at a temperature between 800°C and 938°C. During this step, the surface of wafer 31 is cleaned and made smooth by the etching action of the HCl-H₂ mixture. Other etchants may also be utilized to clean the surface of wafer 31, preferably those etchants which leave a smooth clean surface on the wafer.

Valve 18 is closed, and reaction vessel 11 is then flushed with palladium diffused hydro-

gen from hydrogen source 19. Valve 22 is now opened and the germane in cylinder 21 mixes with the hydrogen from source 19 and passes through the reaction vessel 11. The flow rates of the palladium diffused hydrogen from source 19 and the germane from cylinder 21 are adjusted so that the mixture flowing through the reaction vessel 11 consists of approximately 0.01 to 1.5 volume percent germane, balance hydrogen, and has a total flow rate of approximately ten litres per minute.

In this Example, the rates of flow are adjusted so that the mixture in the reaction vessel 11 consists of approximately 0.03 volume percent germane, balance hydrogen. The germane is thermally decomposed in the reaction vessel 11, and deposits on the exposed surface of wafer 31 as an epitaxial layer. The rate of deposition of the epitaxial layer depends on the concentration of germane in the reaction vessel 11. Accordingly, by controlling this parameter, the epitaxial layer can be made as thick as desired by appropriately varying the time during which the wafer is heated in the germane-hydrogen mixture. In this example, the wafer is heated for one hour in the flowing germane-hydrogen ambient. During this step, the wafer is maintained at approximately 700°C. For higher germane concentrations, higher temperatures up to 938°C are utilized when the substrate is germanium.

Valve 22 is closed, and the reaction vessel 11 is flushed with hydrogen. The electrical power supply to RF coil 12 is interrupted, and the wafer 31 is permitted to cool to room temperature before removal from the apparatus 10.

As a result of this process, wafer 31 now has an epitaxial germanium layer 32 on the exposed surface of wafer 31. Any epitaxial layer on the ends of wafer 31 can be removed, for example, by grinding. The epitaxial layer 32 thus formed is approximately 1/4 mil thick and has an electrical resistivity of approximately 1 ohm-cm. The conductivity type of epitaxial layer 32 depends on the impurities present in the germane, and is generally N-type. Owing to epitaxy, the germanium layer 32 is also monocrystalline; in fact, the crystal lattice of 32 is an extension of the crystal lattice of wafer 31.

Referring now to FIGURE 3c, a P-type conductivity modifier or acceptor may be diffused into a limited portion 34 of epitaxial layer 32 by standard techniques which are known to the semiconductor art, and need not be described here. The portion 34 of epitaxial layer 32 is thus converted to P-type conductivity, and a rectifying barrier or p-n junction 37 is formed at the interface between the P-type portion or region 34 and the N-type bulk of epitaxial layer 32. An N-type conductivity modifier or donor may then be diffused into a limited portion or region 36 of epitaxial layer 32. Region 36, which is completely internal



of P-type region 34, is thereby converted to N-conductivity type, and a rectifying barrier or p-n junction 39 is formed at the interface between the N-type region 36 and the P-type region 34. The structure thus formed may be used as a triode transistor, since it includes an N-type region 36 which can be utilized as an emitter region, a P-type region 34 which can be utilized as a base region, and an N-type region 32 which can be utilized as a collector region. Moreover, the low resistivity wafer 31 can be utilized as a low resistance connection to the collector region 32. The remaining steps of attaching electrical lead wires to the wafer, then mounting and encapsulating the device, are accomplished by standard techniques known to the semiconductor art.

EXAMPLE II

In Example 1 the epitaxial layer deposited was of the same conductivity type as the substrate wafer. The epitaxial layer may also be of conductivity type opposite to that of the substrate wafer, as described in this example: A given conductivity type crystalline semiconductor wafer 41 (FIGURE 4a) is prepared with at least one major face 43. The exact size, shape and conductivity of wafer 41 is not critical. In this example, wafer 41 consists of P-conductivity type germanium, and major face 43 is substantially normal to the (111) crystal axis of the wafer. Wafer 41 is positioned on susceptor block 13 of the apparatus 10 described above in connection with FIGURE 2, and an epitaxial germanium layer 42 is deposited on wafer face 43 in a manner similar to that described above in Example I. However, in the present example, the germane source 21 includes a small amount, of the order of 100 to 1000 parts per million, of a gaseous conductivity type modifier. Suitable materials for this purpose are the hydrides of donors, such as phosphine PH_3 , or arsine AsH_3 . During the decomposition of the germane to form germanium, some of the donor hydride present, (phosphine or arsine, or the like) also decomposes, thereby incorporating donor atoms uniformly throughout the epitaxial layer 42. The epitaxial layer 42 is therefore N-conductivity type, and has a uniform concentration of donor atoms throughout. A rectifying barrier or p-n junction is thus formed at the interface 42 between the P-type wafer 41 and the N-type epitaxial layer 42.

A portion of the epitaxial layer 42 is masked with an acid resist such as paraffin wax or apiezon wax, and the wafer is then immersed in a suitable etchant, such as a mixture of hydrofluoric acid and nitric acid, for a period of time sufficient to remove the unmasked portion of epitaxial layer 42. The wafer is then removed from the etchant and washed in distilled water. The acid resist is removed by means of a suitable solvent, such as carbon tetrachloride or the like, leaving the etched

wafer 41¹ (FIGURE 4b) with a mesa 45 which includes the remaining portion 42¹ of the epitaxial layer, and the remaining portion 43¹ of the rectifying barrier. The resulting structure is readily utilized as a mesa diode by bonding an electrical lead wire to the top of mesa 45, then mounting and encapsulating the unit.

In both Examples, the substrate semiconductor wafer consisted of germanium. The substrate wafer may also consist of a compatible crystalline semiconductive material other than germanium, provided that the crystalline structure of the substrate is the same as that of germanium, and provided that the lattice constant of the substrate is close to those of germanium, e.g. GaAs. Semiconductor devices which include a rectifying barrier or p-n junction between two dissimilar semiconductive materials are known as heterojunction devices.

EXAMPLE III

In this example, a P-conductivity type crystalline wafer 41 (FIGURE 4a) is prepared with one flat polished major face 43, as in Example II but in this Example the semiconductor wafer consists of N-conductivity type gallium arsenide. The crystal structure and lattice constants and thermal coefficient of expansion of gallium arsenide are very similar to those of germanium, so that it is possible to grow an epitaxial germanium layer on a gallium arsenide wafer. Wafer 41 is positioned on susceptor block 13 of apparatus 10 (FIGURE 2), and maintained at a temperature above 700°C while an epitaxial germanium layer 42 is deposited on major face 43 of the N-type gallium arsenide wafer 41. Etching of the gallium arsenide wafer in HCl vapours is not necessary, and it has been found that heating the gallium arsenide wafer in hydrogen for approximately 10 minutes at approximately 700°C just prior to the deposition step is generally sufficient to clean the substrate. In this Example, the germane source 21 includes a few hundred parts per million of borane B_2H_6 , and the epitaxial germanium layer 42 thus deposited is therefore uniformly doped with boron atoms, and hence is of P-conductivity type. A rectifying barrier is formed at or near to the interface between the N-type gallium arsenide wafer 41 and the P-type germanium epitaxial layer 42. The structure thus formed may be used as a heterojunction semiconductor device, for example, a mesa diode, by methods similar to those described above in connection with Example II.

Some of the advantages of the methods described above are that the epitaxial germanium layers deposited thereby have planar mirror smooth surfaces and a high degree of structural perfection. These characteristics give semiconductor devices a high degree of uniformity and reproducibility in their electrical parameters. It is thought that these advantages are ob-





e/

5

10

15

20

25

30

u/

tained because the substrate wafer has been prepared so as to provide a chemically and mechanically clean, smooth surface on which the epitaxial layer is performed in the same apparatus in which the substrate wafer has just been etched, without transferring the wafer, or exposing it to other ambients, and thus avoiding any injury to or change in or contamination of the wafer surface prior to the deposition of the epitaxial layer. Furthermore, a conductivity modifier may be introduced into the epitaxial layer in a uniform fashion. This is advantageous when it is desired to avoid the concentration gradient produced by conventional techniques for introducing a conductivity modifier into an epitaxial layer by diffusion. Moreover, a very abrupt junction may be formed between the substrate wafer and the deposited epitaxial layer.

The above embodiments of the invention have been described by way of example only, and not limitation. If desired, the conductivity type of the various wafer regions described may be reversed, utilizing appropriate acceptors and donors. Other compatible crystalline semiconductors such as silicon and silicon-germanium alloys may be utilized as substrates, instead of gallium arsenide. These materials may be etched prior to the epitaxial deposition step in the same manner as germanium, but utilizing higher temperatures, up to 1100°C.

WHAT WE CLAIM IS:—

1. A method of manufacturing a semiconductor device comprising the steps of: heating a semiconductor wafer in a reaction vessel in the presence of hydrogen; and passing a mixture of germane and hydrogen over the heated surface of the wafer so as to decompose said germane and deposit on said wafer surface as an epitaxial germanium layer.

2. A method as claimed in Claim 1 and including the step of: etching said wafer until

the surface thereof has a high degree of smoothness by flowing HCl gas mixed with H₂ over said surface while heating said wafer at a temperature of between 800°C and 938°C.

3. A method as claimed in Claim 2, wherein said mixture of HCl gas and H₂ consists of 11 volumes H₂ and 2 volumes HCl.

4. A method as claimed in any one of Claims 1 to 3, wherein the mixture of germane and hydrogen consists of hydrogen and between 0.01 and 1.5 volume percent germane.

5. A method as claimed in any one of the preceding claims, wherein the mixture of germane and hydrogen includes between 100 and 1000 parts per million of a substance selected from the group consisting of phosphine and arsine.

6. A method as claimed in Claim 1, wherein said semiconductor wafer is a gallium arsenide wafer, and including the steps of: cleaning the surface of the wafer in hydrogen for 10 minutes at 700°C; and wherein the mixture of germane and hydrogen consists of hydrogen and between 0.01 and 1.5 volume percent germane.

7. A method as claimed in Claim 6, wherein the mixture of germane and hydrogen contains between a few 100 and 1000 parts per million of borane.

8. A method of manufacturing a semiconductor device substantially as hereinbefore described in any one of the three examples.

9. A semiconductor device when made by the method claimed in any one of the preceding claims.

A. M. & WM. CLARK,
Chartered Patent Agents,
5, Stone Buildings,
Lincoln's Inn, London, W.C.2.



1,055,837

e/ 5 tained because the substrate wafer has been prepared so as to provide a chemically and mechanically clean, smooth surface on which the epitaxial layer is performed in the same apparatus in which the substrate wafer has just been etched, without transferring the wafer, or exposing it to other ambients, and thus avoiding any injury to or change in or contamination of the wafer surface prior to the deposition of the epitaxial layer. Furthermore, a conductivity modifier may be introduced into the epitaxial layer in a uniform fashion. This is advantageous when it is desired to avoid the concentration gradient produced by conventional techniques for introducing a conductivity modifier into an epitaxial layer by diffusion. Moreover, a very abrupt junction may be formed between the substrate wafer and the deposited epitaxial layer.

10 The above embodiments of the invention have been described by way of example only, and not limitation. If desired, the conductivity type of the various wafer regions described may be reversed, utilizing appropriate acceptors and donors. Other compatible crystalline semiconductors such as silicon and silicon-germanium alloys may be utilized as substrates, instead of gallium arsenide. These materials may be etched prior to the epitaxial deposition step in the same manner as germanium, but utilizing higher temperatures, up to 1100°C.

u/ 30 WHAT WE CLAIM IS:—

1. A method of manufacturing a semiconductor device comprising the steps of: heating a semiconductor wafer in a reaction vessel in the presence of hydrogen; and passing a mixture of germane and hydrogen over the heated surface of the wafer so as to decompose said germane and deposit on said wafer surface as an epitaxial germanium layer.

2. A method as claimed in Claim 1 and including the step of: etching said wafer until

the surface thereof has a high degree of smoothness by flowing HCl gas mixed with H₂ over said surface while heating said wafer at a temperature of between 800°C and 938°C.

3. A method as claimed in Claim 2, wherein said mixture of HCl gas and H₂ consists of 11 volumes H₂ and 2 volumes HCl.

4. A method as claimed in any one of Claims 1 to 3, wherein the mixture of germane and hydrogen consists of hydrogen and between 0.01 and 1.5 volume percent germane.

5. A method as claimed in any one of the preceding claims, wherein the mixture of germane and hydrogen includes between 100 and 1000 parts per million of a substance selected from the group consisting of phosphine and arsine.

6. A method as claimed in Claim 1, wherein said semiconductor wafer is a gallium arsenide wafer, and including the steps of: cleaning the surface of the wafer in hydrogen for 10 minutes at 700°C; and wherein the mixture of germane and hydrogen consists of hydrogen and between 0.01 and 1.5 volume percent germane.

7. A method as claimed in Claim 6, wherein the mixture of germane and hydrogen contains between a few 100 and 1000 parts per million of borane.

8. A method of manufacturing a semiconductor device substantially as hereinbefore described in any one of the three examples.

9. A semiconductor device when made by the method claimed in any one of the preceding claims.

A. M. & WM. CLARK, 4
Chartered Patent Agents,
5, Stone Buildings,
Lincoln's Inn, 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.

