

PATENT SPECIFICATION

1,109,123

DRAWINGS ATTACHED.



Date of Application and filing Complete Specification:
21 April, 1965. No. 16720/65.

Application made in United States of America (No. 363,228) on
28 April, 1964.

Complete Specification Published: 10 April, 1968.

© Crown Copyright 1968.

Index at Acceptance:—C7 F(1B5, 2Z4, 2Z6, 2Z8, 4P).

Int. Cl.:—C 23 c 11/06.

COMPLETE SPECIFICATION

Deposition of Crystalline Semiconductive Layer on Insulating Substrate.

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 deposition of silicon, and more particularly, to an improved method of depositing a single crystal silicon layer on a sapphire substrate.

Previously silicon has been deposited on a sapphire (alpha-alumina) substrate by flowing a mixture of silicon tetrachloride and hydrogen over the sapphire. At elevated temperatures, silicon tetrachloride is reduced by hydrogen, forming hydrogen chloride and elemental silicon, which is deposited on the substrate. This process has several disadvantages. First, the silicon deposit thus formed by the reaction between silicon tetrachloride and hydrogen generally consists of several single crystal areas, with grain boundaries between them, whereas it is desirable for many applications to have the entire semiconductive layer constitute a single crystal area, without any grain boundaries. Furthermore, the silicon layer is generally of N-type conductivity, whereas it is desirable for some applications to use a semiconductive layer of P-type conductivity on an insulating substrate.

Accordingly, it is an object of this invention to provide an improved method of depositing single crystal silicon on sapphire substrates.

The practice of the invention comprises preparing a sapphire substrate and maintain-

ing the substrate at about 1000°C to about 1150°C while flowing silane over the substrate to decompose the silane and deposit a layer of single crystal silicon on the substrate.

Figure 1 is a flow diagram of a method according to the invention.

EXAMPLE I

A body of single crystal alumina (sapphire) is prepared as the substrate. The exact size and shape of the body is not critical. In this example, the sapphire body is a disc about 0.020 inch thick and 0.375 inch diameter. Preferably the exposed surface of the crystal is clean, smooth and of a predetermined crystal orientation. Single crystal alumina forms a lattice defined by three crystal axes, known as the A, B and C axes. It has been found advantageous to cut the sapphire disc with the major faces of the disc at an angle of about 60° to the "C" axis of the crystal lattice so that a 2243 crystal face is exposed. While the exact mechanism for the improved result thus obtained is not certain, it is known that when sections of a hexagonal crystal are made in different ways, the spacing and density of the crystal atoms in the exposed crystal face will vary. By cutting and lapping a major face of the sapphire disc at a 60° angle to the "c" axis to expose a 2243 crystal face, the spacing of atoms in this exposed crystal face becomes close to the spacing of atoms in single crystal silicon. It is presently believed that this close match in lattice distance produces the best single crystal layers. Other orientations of the crystal which provide a similar lattice spacing may be used as well.

Apparatus 10 (Figure 2) comprises a water-cooled quartz furnace tube 11 pro-

vided with an RF heating coil 12. A helium tank 16 is connected to the furnace tube 11 by a quartz line 22 suitably equipped with valves 23, liquid traps 24, and flow meters 25. Hydrogen source 17 is similarly connected to furnace tube 11. Before reaching the furnace tube, the hydrogen is purified by passing it through a palladium diffuser 18.

Gas tanks 19, 20 and 21 are also connected to furnace tube 11 by quartz lines 22. Tank 19 contains a mixture of hydrogen and about 1 to 5 volume percent silane. In this example, tank 19 contains a mixture of 97 volume percent hydrogen and 3 volume percent silane. Tank 20 contains a mixture of hydrogen and gas which induces N-type conductivity in silicon. In this example, tank 20 contains hydrogen with about 50 parts per million phosphine. Tank 21 contains a mixture of hydrogen and gas which induces P-type conductivity in silicon. In this example, tank 21 contains hydrogen with about 50 parts per million diborane.

The polished sapphire substrate thus prepared 15 (Figure 2) is positioned in the water-cooled furnace tube 11 on a silicon susceptor block 14 with its smooth face of the substrate 15 uppermost, in contact with incoming vapors. The apparatus 10 is flushed first with helium from tank 16, then with hydrogen from tank 17. The sapphire is heated in an ambient of flowing hydrogen for about 15 minutes at about 1250°C. This treatment cleans the surface of the sapphire substrate. The sapphire is then cooled to about 1000–1150°C, while maintaining the flow of hydrogen.

The silane-hydrogen mixture from tank 19 is now passed into the furnace tube 11. Pure silane tends to decompose with explosive violence when exposed to oxygen, but silane diluted with hydrogen decomposes smoothly to form hydrogen and elemental silicon. The former passes out of furnace tube 11 through the gas exit 26, while some of the latter deposits on the polished face of sapphire disc 15 as a monocrystalline layer. The rate of deposit of the silicon layer varies with the concentration of silane in the mixture, the rate of flow of the mixture, and the temperature in the furnace.

After the monocrystalline silicon layer has obtained the desired thickness, which may for example be in the range of about 1 to 50 microns, the flow of the silane-hydrogen mixture from tank 19 is terminated. Advantageously, the sapphire substrate 15 is cooled to room temperature in a hydrogen ambient without removing it from the furnace tube 11. For best results, a cooling rate of about 25°C per minute is preferred.

Silicon layers thus deposited on the polished face of the sapphire substrate have been found to be free of grain boundaries, and of good single crystal quality through-

out, as determined by both Laue X-ray reflection techniques and electron diffraction techniques. A fairly high degree of crystal-line perfection is shown by the presence of Kikuchi lines in the electron diffraction pattern of the silicon layers.

Another feature of the silicon layers formed as described in this example is that they are uniformly of P-type conductivity, whereas silicon layers formed by prior art methods are reported to be all N-type. For certain types of devices, it is preferred to use a P-type semiconductive layer.

It appears probable that the improved results obtained by the method of this invention may be due to the fact that the only reaction product other than silicon in this method is hydrogen, which is a harmless diluent in this system. Furthermore the deposition temperature used herein is much higher than that temperature required merely to decompose silane. The use of a deposition temperature in excess of the minimum required improves the quality of the silicon layer.

EXAMPLE II

The P-type monocrystalline layer deposited as in Example I above, in the absence of any conductivity modifier, exhibits electrical resistivity in the range of about .01 to 20 ohm-cm. If it is desired to deposit P-type monocrystalline silicon layers with low resistivity, the method described in Example I may be generally followed, with the addition of an acceptor. When the silane-hydrogen mixture from tank 19 is flowing into the furnace tube 11, the valve on tank 21 is opened so that some of the diborane hydrogen mixture also enters furnace tube 11. As a result, the silicon layer deposited on the sapphire substrate contains some boron atoms, thereby increasing the concentration of holes (positive charge carriers) in the silicon layer, and decreasing the electrical resistivity of the layer. The level of boron doping in the silicon layer may be varied as desired by monitoring the amount of diborane-hydrogen mixture flowing into furnace tube 11.

EXAMPLE III

If desired, N-type monocrystalline silicon layers may be deposited instead of P-type layers. The method described in Example I is generally suitable for this purpose, with one change. When the silane-hydrogen mixture from tank 19 is flowing into furnace tube 11, the valve on tank 20 is opened, so that some of the phosphine-hydrogen mixture also enters the furnace tube 11. The silicon layer thus deposited on the sapphire substrate contains sufficient phosphorus atoms to be of N-type conductivity.

Monocrystalline silicon layers deposited on silicon substrates as described above have

been utilized to fabricate insulated-gate field-effect devices. Transconductances as high as 1000 micro-mho were obtained with such devices. This is within a factor of two of the highest transconductance values obtained for devices of equal dimensions on the best bulk-grown single crystal silicon, and is equal to the transconductance values frequently obtained with ordinary bulk single crystalline silicon.

WHAT WE CLAIM IS:—

1. The method of depositing a single crystal silicon layer on an exposed surface of a sapphire substrate, comprising the steps of maintaining said substrate at a temperature of 1000°C to 1150°C while flowing silane over said surface thereby to decompose said silane and deposit a layer of single

crystal silicon of a high degree of crystalline perfection on all areas of said surface.

2. A method according to claim 1 wherein said silane is present in about 1—5 volume percent in hydrogen.

3. A method according to claim 1 wherein said exposed surface has a spacing of atoms close to that of single crystal silicon.

4. A method of depositing a single crystal silicon layer on an exposed surface of a sapphire substrate, substantially as described with reference to the accompanying drawings.

ANDREWS & BYRNE, 
Agents for the Applicants,
Chartered Patent Agents,
104/5 Newgate Street,
London, E.C.1.

been utilized to fabricate insulated-gate field-effect devices. Transconductances as high as 1000 micro-mho were obtained with such devices. This is within a factor of two of the highest transconductance values obtained for devices of equal dimensions on the best bulk-grown single crystal silicon, and is equal to the transconductance values frequently obtained with ordinary bulk single crystalline silicon.

WHAT WE CLAIM IS:—

1. The method of depositing a single crystal silicon layer on an exposed surface of a sapphire substrate, comprising the steps of maintaining said substrate at a temperature of 1000°C to 1150°C while flowing silane over said surface thereby to decompose said silane and deposit a layer of single

crystal silicon of a high degree of crystalline perfection on all areas of said surface.

2. A method according to claim 1 wherein said silane is present in about 1—5 volume percent in hydrogen.

3. A method according to claim 1 wherein said exposed surface has a spacing of atoms close to that of single crystal silicon.

4. A method of depositing a single crystal silicon layer on an exposed surface of a sapphire substrate, substantially as described with reference to the accompanying drawings.

ANDREWS & BYRNE,
Agents for the Applicants,
Chartered Patent Agents,
104/5 Newgate Street,
London, E.C.1.

Printed for Her Majesty's Stationery Office by Burgess & Son (Abingdon), Ltd.—1968.
Published at The Patent Office, 25 Southampton Buildings, London, W.C.2,
from which copies may be obtained.



* C L M S *