

March 12, 1968

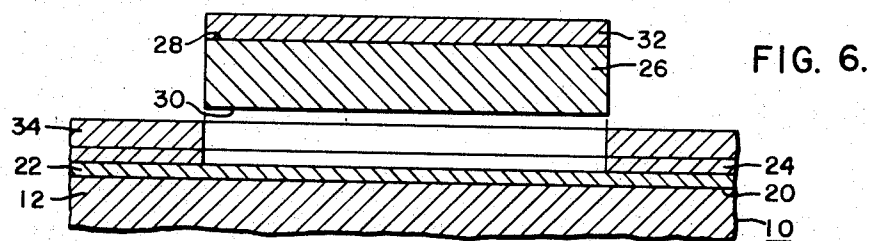
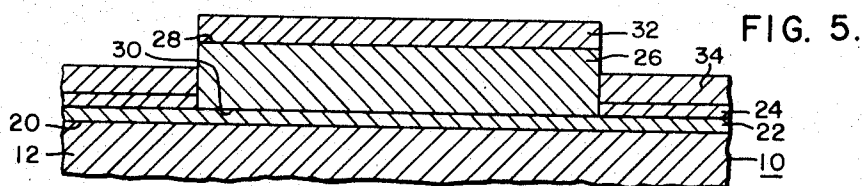
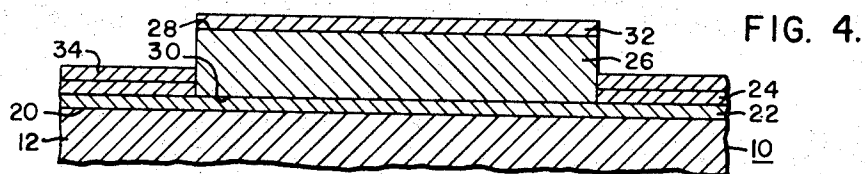
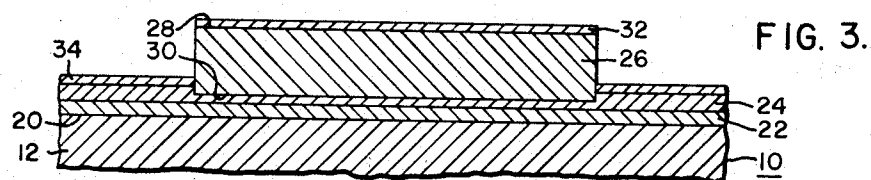
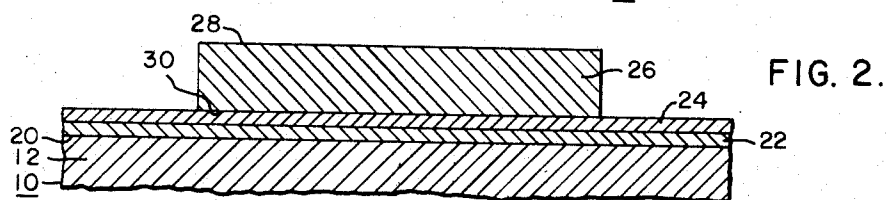
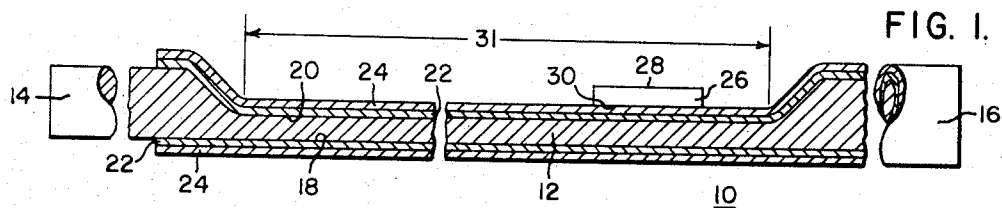
TING LI CHU

3,372,671

APPARATUS FOR PRODUCING VAPOR GROWTH OF SILICON CRYSTALS

Filed May 26, 1965

2 Sheets-Sheet 1



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2 Sheets-Sheet 2

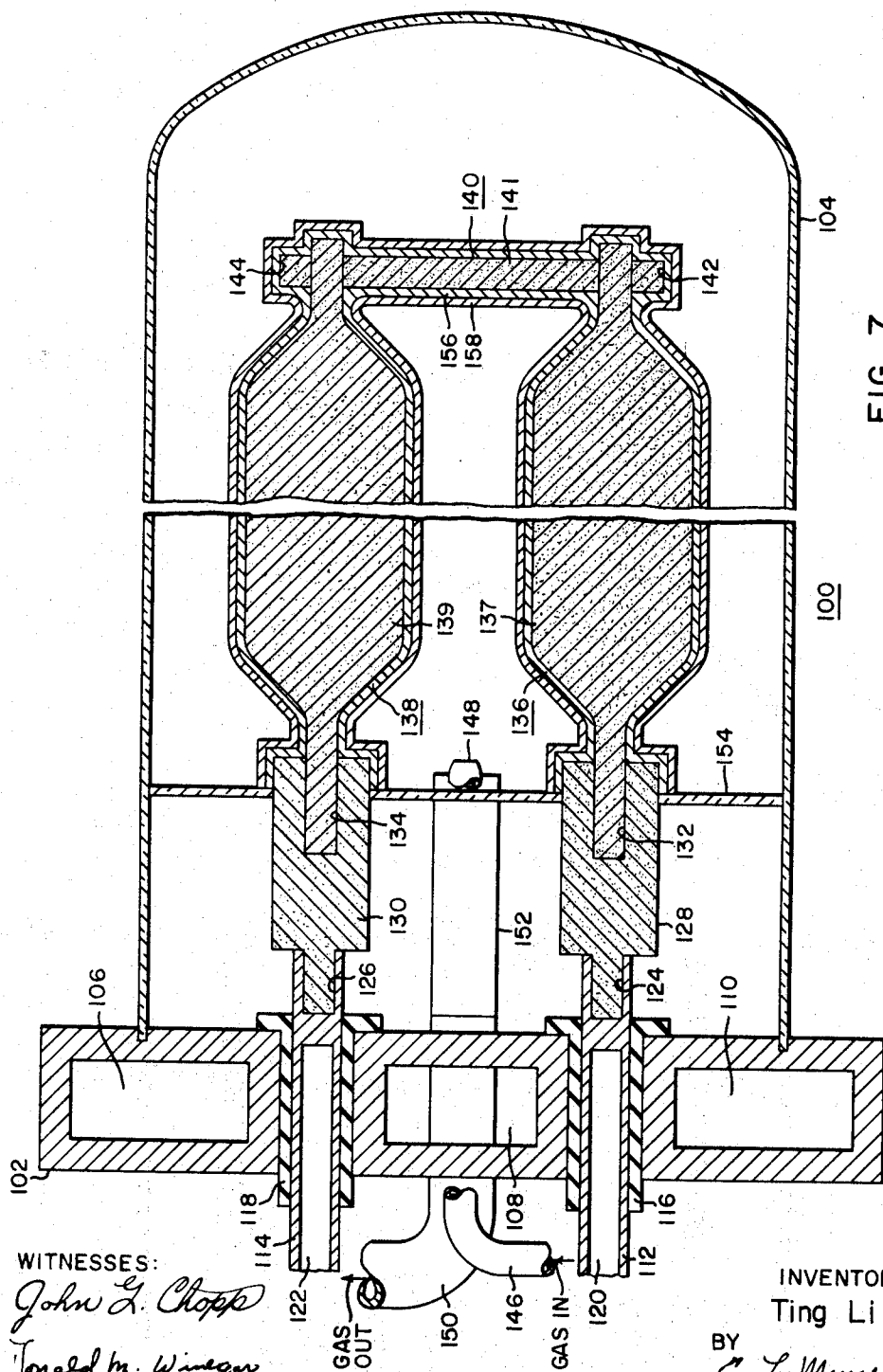


FIG. 7.

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ABSTRACT OF THE DISCLOSURE

Siliconized heater strips are employed in silicon vapor growth apparatus. Silicon is deposited on a heater strip heated to a temperature higher than the melting point of silicon to form an impervious coating of a silicide of the material comprising the heater. A layer of silicon is then grown on the silicide coating.

This invention relates to apparatus employed in the epitaxial growth of semiconductor materials.

Heretofore, in the growth of epitaxial silicon on a single crystal silicon substrate, the substrate was supported on a silicon heater strip in a furnace and a gas consisting of hydrogen and a halogenated silane was decomposed in the furnace, the silicon resulting from the decomposition deposited on the substrate.

Hydrogen chloride, formed during the growth process, diffused in between the substrate and the heater strip. Since the silicon heater strip was at a slightly higher temperature than the substrate, hydrogen chloride transferred silicon from the heater strip to the substrate. Unless the growth time was very short, the substrate and the heater strip grew together. It was apparently for this reason that the maximum thickness of silicon crystals grown by the vapor growth technique has never been reported as exceeding 0.003 inch.

An object of this invention is to provide an improved heater strip for use in apparatus for carrying out the terminal reduction of a halogenated silane with hydrogen.

Another object is to provide a heater strip having a first coating of a silicide of the material which comprises the core of the heater strip and a second coating consisting of silicon deposited on the first coating.

Other objects of the invention will, in part, be obvious and will, in part, appear hereinafter.

For a better understanding of the nature and objects of the present invention reference should be had to the following detailed description and drawings, in which:

FIGURE 1 is a side view, partially in cross-section of a siliconized heater strip made in accordance with the teachings of this invention;

FIGS. 2 through 6 are enlarged cross-sectional views illustrating the epitaxial growth of material on a substrate disposed on a siliconized heater strip made in accordance with the teachings of this invention; and

FIG. 7 is a cross-sectional view of a reactor chamber constructed in accordance with the present invention.

In accordance with the present invention and in attainment of the foregoing objects, there is provided an improved heater strip suitable for use in the epitaxially growing of a material on a substrate. The heater strip comprises a core of a material selected from the group consisting of carbon, molybdenum, tantalum, tungsten and base alloys thereof.

The heater strip has a first coating comprising a silicide of the material of the core disposed on all exposed surfaces of the core. A second coating consisting of silicon is disposed on the first coating.

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With reference to FIG. 1, there is shown a siliconized heater strip 10 made in accordance with the teachings of this invention.

The heater strip 10 comprises a core 12 having two integral cylindrical end projections 14 and 16, a bottom surface 18 and a top surface 20. The core 12 comprises a material selected from the group consisting of carbon, molybdenum, tungsten, tantalum and base alloys thereof.

A first coating 22, comprising a silicide of the material utilized for making the core 12, is disposed on both the bottom surface 18 and the top surface 20 of member 12. A second coating 24 consisting of silicon is disposed on and completely surrounds the first coating 22.

The heater strip 10 is primarily for use in apparatus for the deposition of silicon resulting from the thermal reduction of a halogenated silane with hydrogen and the deposition of the silicon on suitable substrates, such, for example, as single crystal silicon. The strip 10, as shown in FIG. 1, is designed for use in a horizontally oriented vapor growing apparatus. It is to be understood, however, that the physical shape of the strip 10 is to be determined by the apparatus in which it will be used.

The product of the cross-sectional area and the surface area per unit length of the core 12 is constant. This constant product is necessary to produce a uniform temperature on all regions of the heater strip 10. A uniform temperature on all regions is required since a process utilizing the strip 10 for the epitaxial growth of silicon resulting from the thermal decomposition of a halogenated silane with hydrogen incorporates a high temperature range. This high temperature range may cause the coatings 22 and 24 to melt should "hot spots" occur in regions of the strip 10. A "hot spot" is a region of the strip 10 whose actual temperature is greater than the temperature of the remainder of the strip 10.

Carbon, in the form of graphite, is particularly suitable for making the strip 10. However, graphite is by nature porous and at the temperatures required for the vapor deposition of silicon it will react with hydrogen. Absorbed gases of the graphite upon heating are liberated from the porous structure and severe contamination of the silicon, or any other vapor grown material, occurs.

A heater strip having a core of graphite, similar to the strip 10, when constructed in accordance with the teachings of this invention will not contaminate vapor grown materials at high temperatures. The first coating 22 comprises silicon carbide which seals the pores of the surfaces 18 and 20. The coating 22 should be of sufficient thickness so that no graphite is exposed during use. The coating 22 therefore contains the absorbed gases within the core 12. As will be explained in detail hereinafter the coating 22 also prevents the substrate, upon which the vapor grown material is deposited, from adhering to the heater strip 10.

A suitable substrate 26 such, for example, as a single crystal silicon wafer, and having a top surface 28 and a bottom surface 30, is disposed on the second coating 24 consisting of silicon within a flat planar region 31 of the strip 10. During the vapor growth process, the silicon of the coating 24 beneath the substrate 26 is transferred to the bottom of the substrate 26. This process is shown in FIGS. 2 through 7.

With reference to FIG. 2 there is shown the substrate 26 of single crystal silicon, suitably prepared by methods known to those skilled in the art, disposed on the coating of silicon 24, which surrounds and completely covers coating 22 which in turn surrounds the core 12, prior to beginning the deposition of silicon by the vapor growth process.

With reference to FIG. 3 there is shown the substrate 26 after the vapor growth of silicon has been practiced for a period of time.

An epitaxial layer 32 of silicon has been deposited on the top surface 28 of the substrate 26. At the same time a coating 34 of silicon has been deposited on the silicon coating 24 not covered by the substrate 26 and a portion of the coating 24 beneath the substrate 26 is transferred to, and becomes a continuation of, the bottom surface 30.

With reference to FIG. 4, the vapor growth process has continued for a sufficient length of time whereby all of the silicon in the silicon coating 24 immediately beneath the bottom surface 30 of the substrate 26 has been transferred to the substrate 26. The substrate 26 is now disposed on the coating 22 of silicon carbide.

With reference to FIG. 5, continued vapor growth processing has increased the thickness of the coatings 32 and 34. No further growth on the bottom surface 30 of the substrate 26 has occurred. The coating 22 of silicon carbide is not transferred to the substrate 26.

With reference to FIG. 6, the substrate 26 with its silicon vapor growth coating 32 is shown removed from the strip 10. The substrate 26 does not adhere to the silicon carbide coating 22. Removal of the substrate 26 leaves a recess in the silicon coatings 24 and 34 on the core 12. The epitaxial layer 32 is capable of being produced in a thickness exceeding 0.003 inch, the final thickness being limited only by the duration of the process run.

The heater strip 10 is reusable. After a vapor growth run the strip 10 has the remaining portions of the initial silicon layer 24 and newly deposited layer 34 removed by conventional etching technique known to those skilled in the art and employing anhydrous hydrogen chloride at from 1200° C. The process for depositing silicon on the strip 10 is then repeated and a new vapor growth run started.

With reference to FIG. 7, there is shown a vapor growth apparatus 100 incorporating siliconized heater strips made in accordance with this invention. The preferred orientation of the apparatus 100 is to operate it in a horizontal plane since suitable substrates need only be placed in the apparatus 100 without any physical restraining being required.

The apparatus 100 comprises a base 102 on which is mounted a cylindrical reaction vessel 104 preferably constructed of quartz. It will be appreciated that a gas tight seal is maintained between the vessel 104 and the base 102.

The base 102 comprises a material such, for example, as silver plated brass. Passages 106, 108 and 110 permit the circulation of a coolant such as water through the base 102 during operation of the apparatus 100.

Passing through the base 102 are electrodes 112 and 114, for example, of silver, which are electrically insulated from the base 102 by bushings 116 and 118 respectively. The bushings 116 and 118 also provide a gas tight seal. The electrodes 112 and 114 contain passages 120 and 122, respectively, for circulating a coolant.

In the upper ends of the electrodes 112 and 114 are provided recesses 124 and 126 respectively in which are placed pure graphite electrodes 128 and 130. In the opposite end of each of the electrodes 128 and 130 are elongated recesses 132 and 134 respectively. One end of each heater strip 136 and 138 is closely fitted into the recesses 132 and 134 respectively. The opposite ends of the strips 136 and 138 are joined together by a bridging strip 140 by snugly fitting the ends into recesses 142 and 144 respectively.

The heater strips 136 and 138 are made in accordance with the teachings of this invention. Each heater strip 136 and 138 comprise a core 137 and 139, respectively, of a material selected from the group consisting of carbon, molybdenum, tungsten, tantalum and base alloys thereof. The bridging strip 140 comprises a core 141 of the same material as the cores 137 and 139 of the heater strips 136 and 138 respectively. Like the heater strips 136

and 138, the bridging strip 140 must have a constant product of the cross-sectional area and the surface area per unit length.

Electrical current, either A.C. or D.C., may be applied to the electrodes 112 and 114, respectively, from which it passes to the graphite electrodes 128 and 130, respectively, thence to the heater strips 136 and 138 respectively and thence to be conducted by the bridging strip 140.

Passing through the base 102 is a gas inlet tube 146, preferably of silver, with an extension tube 148, preferably of quartz. The gas inlet tube 146 and the extension 148 are disposed symmetrical with respect to the two heater strips 136 and 138. The gas inlet tube 146 and the extension 148 are located below the plane defined by the heater strips 136 and 138.

A gas outlet tube 150, preferably of silver, having an extension tube 152, preferably of quartz is symmetrically disposed on the opposite side of the plane defined by the heater strips 136 and 138.

To minimize any possible contamination from the metal parts if the apparatus 100 a multiple apertured plate 154, preferably of quartz, having an outer periphery less than the inner periphery of the vessel 104 is disposed between the base 102 and the heater strips 136 and 138. The electrodes 130 and 128, as well as the tube extensions 148 and 152 pass through the apertures in the plate 154. There need not be a gas tight seal between the components and the plate 154.

A preferred method of producing the siliconized heater strips 136 and 138 is to coat them after they are assembled into the apparatus 100.

The respective graphite cores 137 and 139 of the heater strips 136 and 138 and the graphite core 141 of the bridging strip 140 are heated to a temperature exceeding the melting point of silicon. The temperature of 1475° C. $\pm$ 25° C. has been found to be very satisfactory. The cores 137, and 139 and 141 are kept at this temperature for approximately 2 hours. During this time at the elevated temperature, hydrogen gas flowing at a rate of approximately 6 liters per minute is continually circulating through the reactor vessel 104. The hydrogen cleans the exposed surfaces of the cores 137 and 139 as well as the exposed surfaces of the core 141 of the bridging strip 140.

After approximately two hours, a reactant gas mixture of a halogenated silane compound and hydrogen is introduced into the reactant vessel. Suitable halogenated silane compounds are silicon tetrachloride, trichlorosilane, dichlorosilane and silicon tetraiodide. Hereafter, specific reference will be made to trichlorosilane, HSiCl_3 , but it will be understood other halogenated silanes may be employed in a similar manner.

The reactant gas mixture comprises hydrogen flowing at a rate of from 5 to 50 liters per minute. Trichlorosilane is introduced into the hydrogen at a rate which produces a reactant gas mixture comprising from 1% to 5% by volume of trichlorosilane and the remainder is hydrogen. The preferred condition is a hydrogen flow rate of 10 liters per minute into which trichlorosilane is introduced so as to comprise 2% of the total volume of gas.

Care is taken to assure the deposit of silicon is not occurring too fast and thereby preventing the reaction with carbon from occurring and failing to seal the pores of the graphite strips 136, 138 and 140. Under the specified conditions, a coating 156 of silicon carbide is formed on the cores 137, 139 and 141 as well as the protruding surfaces of the graphite electrodes 128 and 130. The coating 156 seals the pores of the graphite surfaces and provides a smooth continuous surface for the next coating. A thickness of from 1 to 10 mls is deposited. The minimum and maximum thickness are purely an operator's judgment and depends upon how clean his graphite components were initially.

The temperature of the strips 136, 138 and 140 is

then lowered to $1075^{\circ}\text{C} \pm 25^{\circ}\text{C}$. The same reactant gas mixture is introduced into the reactor vessel 104 and a coating 158 of silicon is deposited on the coating 156 of silicon carbide. A thickness of from 2 to 5 mils has been found sufficient.

A suitable substrate is prepared by means known to those skilled in the art. The substrate comprises single crystal semiconductor material such, for example, as p-type silicon. Silicon epitaxially grown in the apparatus 100 normally has n-type semiconductivity.

The substrate is placed on the top surface of one of the siliconized heater strips 136 or 138 of the apparatus 100. The substrate is brought to a temperature of $1230^{\circ}\text{C} \pm 10^{\circ}\text{C}$ and hydrogen gas flowing at the rate of approximately 6 liters per minute is passed through the reactor chamber for $\frac{1}{2}$ to 3 hours. The hydrogen removes any oxide film from the top surface of the substrate.

The gas has a minimum velocity of 10^6 centimeters per second. The gas travels the length of the reactor vessel 104 and impinges on the closed end. Before impingement, the transverse components of the gas mixture flow velocity are small. After impingement, the directed velocity of the gas molecules is diminished and the gas travels over the exposed surface of the substrate with very good turbulence. When the gas is a mixture of two or more gases, good mixing will occur over the exposed surface of the substrate. After passing over the substrate the gas is exhausted through the tube 150 and its extension 152.

The temperature of the substrate is then reduced to $1155^{\circ}\text{C} \pm 25^{\circ}\text{C}$. A reactant gas mixture, having a minimum velocity of 10^6 centimeters per second is introduced into the reactor vessel 104. The reactant gas comprises hydrogen and trichlorosilane. The flow rate of hydrogen varies from 2 to 50 liters per minute, with the preferred flow rate being 10 liters per minute. Trichlorosilane comprises 1% to 5% by volume of the total reactant gas mixture. The preferred reactant gas mixture comprises 2% trichlorosilane by volume. The rate of growth of the resulting silicon deposited by the thermal reduction of trichlorosilane by hydrogen is from 30 microns to 200 microns per hour with a growth of 10 microns per hour occurring with the preferred gas reactant mixture.

Epitaxial grown layers of doped semiconductor material are also produced in the apparatus 100. For example, boron tribromide when simultaneously introduced into the reactant gas mixture of hydrogen and trichlorosilane produces an epitaxial growth of p-type silicon. Similarly other compounds comprising metallic halides of dopant material may be used.

The substrate temperatures reported in this specification were measured with a micro-optical pyrometer. The true temperature, after correcting for the emissivity of silicon and the reflection losses at the wall of the reactor vessel is probably 60°C . to 80°C . above the measured temperature.

Example I

An apparatus for vapor growing silicon and comprising siliconized heater and bridging strips having cores of graphite was constructed in accordance with the teachings of this invention.

The graphite cores of the heater and bridging strips were heated to a temperature of $1480^{\circ}\text{C} \pm 10^{\circ}\text{C}$. The temperature was held for two hours while hydrogen flowing at a rate of 6 liters per minute was passed through the reactor vessel.

The temperature of the heater and bridging strips is maintained at $1480^{\circ}\text{C} \pm 10^{\circ}\text{C}$ and a reactant gas mixture of hydrogen and trichlorosilane is introduced into the reactor vessel. The hydrogen flow rate was 10 liters per minute with trichlorosilane being 2% by volume of the total reactant gas. A layer of silicon carbide was formed on all exposed graphite surfaces with a thickness of approximately 0.004 inch in one hour.

The temperature of the heater and bridging strips were lowered to $1090^{\circ}\text{C} \pm 10^{\circ}\text{C}$ and the same reactant gas mixture was introduced into the reactor vessel under the same flow conditions. A layer of silicon 0.004 inch in thickness was deposited on the layer of silicon carbide.

A single crystal p-type silicon substrate $1\frac{1}{8}$ inches in diameter and 0.02 inch in thickness was prepared by known standard mechanical lapping and chemical polishing techniques. The substrate was then placed on one of the siliconized graphite heater strips in the reactor vessel.

The substrate was brought to a temperature of $1220^{\circ}\text{C} \pm 10^{\circ}\text{C}$ as observed with a micro-optical pyrometer. Hydrogen gas flowing at a rate of 6 liters per minute was flowed through the reactor chamber for one hour to remove the surface oxide layer from the substrate.

The temperature of the substrate was reduced to $1140^{\circ}\text{C} \pm 10^{\circ}\text{C}$ as observed with a micro-optical pyrometer. A reactant gas mixture of hydrogen and trichlorosilane was introduced into the reactor vessel. The hydrogen flow was 10 liters per minute. Trichlorosilane was 2% by volume of the reactant gas mixture. The reactant gas flow was continued for $1\frac{1}{2}$ hours.

All gases entered the reactor vessel with a velocity in excess of 10^6 centimeters per minute.

Upon completion of the vapor growth run the substrate and its vapor grown silicon was easily removed from the heater strip. A recess remained in the silicon layer of the heater strip when the substrate was removed.

The silicon was a good epitaxially film growth of good crystalline perfection, being essentially free from stacking faults and microscopic imperfections. The epitaxial growth of silicon was 0.005 inch in thickness having a resistivity of 20 ohm-centimeter and n-type semiconductivity. The variation in the thickness of the epitaxial growth did not exceed 5% across the entire surface of the substrate.

A diode was fabricated from the epitaxial silicon by conventional techniques. The ohmic contacts were $\frac{3}{4}$ of an inch in diameter. The breakdown voltage was 950 volts at room temperature. The reverse current of the diode prior to the voltage breakdown was less than 1 milliamperes.

Example II

The process described in Example I was duplicated except that the substrate comprised single-crystal n-type silicon and boron tribromide was introduced into the reactant mixture at a rate of 10^{-5} moles/minute during the growth process.

The substrate was easily removed from the siliconized graphite heater strip. The epitaxial growth of silicon contained the dopant boron and had p-type semiconductivity. The epitaxial growth was 0.006 inch in thickness. The variation in the thickness of the epitaxial growth did not exceed 5% across the entire surface of the substrate. The growth was of good crystalline perfection being essentially free of stacking faults and microscopic imperfections.

A diode was fabricated from the resulting semiconductor device by conventional fabrication techniques. The contacts were $\frac{3}{4}$ of an inch in diameter. The breakdown voltage of the semiconductor device was 1500 volts.

While the invention has been described with reference to particular embodiments and examples, it will be understood of course, that modifications, substitutions and the like may be made therein without departing from its scope.

I claim as my invention:

1. In an apparatus for carrying out the thermal reduction of a halogenated silane with hydrogen in a reactor chamber and depositing silicon so produced on a substrate disposed on a heater strip; said heater strip comprising a core comprising a material selected from the group consisting of carbon, tantalum, tungsten,

molybdenum and base alloys thereof; a first coating of a silicide of the same material of the core disposed on all exposed surfaces of said core; a second coating consisting of silicon disposed on said first coating; said substrate being placed only upon said second coating; said heater strip having a uniform cross-sectional area; said apparatus including a gas inlet tube located below the plane defined by said heater strip and a gas outlet tube located above the plane defined by said heater strip.

2. The apparatus of claim 1 wherein the material of said core comprises carbon.

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