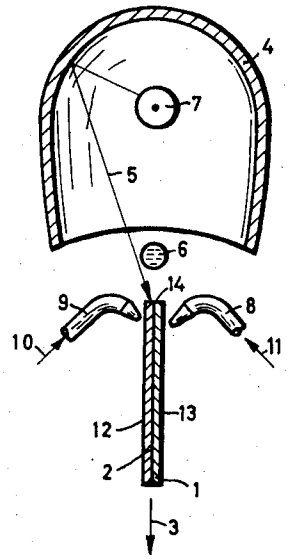
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METHOD OF PULLING A DENDRITIC CRYSTAL FROM A VAPOR ATMOSPHERE

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METHOD OF PULLING A DENDRITIC CRYSTAL FROM A VAPOR ATMOSPHERE

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Our invention relates to a method for the production of monocrystalline, particularly thin, bodies of silicon or other semiconductor substance, by thermal decomposition of a gaseous compound of the semiconductor substance and precipitation onto a carrier.

It is an object of the invention to solve the problem of producing monocrystalline semiconductor bodies in the shape of extremely thin plates, wafers, or coatings. To this end, and in accordance with a feature of our invention, we pyrolytically precipitate the semiconductor substance upon a narrow side of a plate-shaped seed crystal which possesses at least one twin plane extending parallel to its broad surface, this narrow side or edge of the monocrystalline plate being heated to the pyrolytic dissociation temperature. The seed crystal is so oriented that the rate of growth in the direction of the broad surface is considerably greater than at a right angle thereto.

According to another, preferred feature of our invention, the seed crystal, during precipitation and growth of the semiconductor substance, is continuously pulled out of the reaction zone at a speed corresponding to the growth rate of the semiconductor on its narrow-edge side. As a result, our method permits the production of plate-shaped bodies of any desired length.

The method according to the invention results in a dendrite-type growth mechanism due to rapid crystalline growth from the gaseous phase. The rate of growth is greater than in the heretofore known pyrolytic growing methods for producing semiconductor layers from the gaseous phases by precipitation upon a rod or plate-shaped carrier consisting of the same semiconductor substance. The twin planes extending in the direction of growth serve as the origin for the attachment of new rows of atoms.

A further explanation and description follows with reference to a particularly favorable embodiment of the method represented on the accompanying drawing.

The illustration shows a plate-shaped seed crystal **1**, consisting for example of silicon, having a twin plane **2** extending parallel to its broad surfaces **12** and **13** and hence parallel to the "plane" of the plate. This direction is perpendicular to the plane of the illustration. A seed crystal with several parallel twin planes, however, is applicable for use as a carrier. Such a seed crystal can be obtained, for example, by supercooling a melt of the solid material to a temperature at which a portion of the melt freezes. This results in the formation of dendritic crystals with one or more internal twin planes.

In the production of bodies having a cubic crystal lattice, for example the production of silicon bodies, the seed crystal being employed is to be so oriented that its broad surfaces **12** and **13** extend in the direction of the (111) plane and whose narrow side (edge) **14**, extending perpendicularly thereto, is oriented in the (211) plane. The rate of growth of a seed crystal thus oriented is much greater in the direction of planes **12**, **13** than perpendicularly thereto. A seed crystal so oriented is disposed in an atmosphere that contains a gaseous compound of the semiconductor substance to be produced by dissociation, for example in a reaction gas mixture cinsisting of silicochloroform ($SiHCl_3$) and hydrogen. This atmosphere is

replenished as depleted. Other compounds are also applicable, for example hydrogen compounds of silicon (such as SiH_4) or other halogenides (for example $SiCl_4$ or SiI_4). With the seed crystal thus mounted, the narrow side **14** of the seed **1** is heated by means of a heating device to a temperature which is equal to or greater than the dissociation temperature of the gaseous compound of the semiconductor substance so that the semiconductor substance, silicon in the above-mentioned example, is precipitated onto the narrow side **14** of the crystal seed. Suitable dissociation temperatures for silicon are above 850° C. and below the melting point of silicon i.e. 1420° C. The ratio of reactants may vary within reasonable limits. One illustrative range is about 5% by volume of $SiHCl_3$ and 95% by volume of hydrogen. Under these conditions the twin plane, at the location where it emerges at the surface of the narrow side of the carrier, acts as an origin for the attachment of the atom rows. Consequently, a monocrystalline semiconductor layer grows onto the narrow side **14** of the seed. By pulling the crystal seed out of the reaction zone in the direction of the arrow **3** (by means such as shown in application Serial No. 139,400, filed September 20, 1961) at a speed corresponding to the rate of growth of the semiconductor material on the narrow side of the carrier, a thin, plate-shaped semiconductor body of any desired length is formed.

In the above-described example, the rate of growth is approximately 1 mm. per minute. The carrier is pulled out of the reaction zone in the direction of arrow **3** at the same speed. However, the rate of growth, depending upon the thickness of the layer being precipitated, can also be increased by a factor 10 to 100, or it may also be somewhat below the value mentioned above by way of example.

An infrared radiator **7** is employed in the illustrated embodiment for heating the narrow side **14** of the carrier to the dissociation temperature. The radiation source **7** is mounted in a radiation-reflecting shield **4** so that the heat rays, of which one is schematically represented and denoted by **5**, impinge essentially upon only the narrow side of the plate-shaped carrier **1** and heat this narrow side to the necessary temperature. However, the heating of the narrow side of the carrier can also be effected by an electric gas discharge which is maintained between the narrow side of the carrier and an electrode arranged within the reaction space.

In order to prevent the growth of crystalline material in the direction perpendicular to the planes of the plate to the greatest possible extent, that is, to avoid the growing plate from becoming thicker than the plate-shaped seed, the broad surfaces of the carrying seed, according to another feature of the invention, are contacted by a flowing current of gas. This can be effected, for example, by means of two nozzle-shaped deflector sheets, illustrated at **8** and **9**, which extend perpendicularly to the plane of illustration, at least over the entire width of the plate-shaped carrier **1**. The nozzles are traversed by an inert gas, for example nitrogen, in the direction indicated by respective arrows **10** and **11**. The nitrogen flow impinging upon the broad surfaces **12** and **13** that extend perpendicular to the narrow edge side **14** dilutes the reaction gas mixture at the broad surface planes thereby reducing the reaction at these surfaces. The cooling of the surface planes likewise effected by the auxiliary gas has an additional reaction-impeding effect and thereby contributes to preventing a growth of the semiconductor substance at a right angle, in the plane of illustration, to the surface planes **12** and **13**.

In some cases it is desirable, for preventing the travel of a portion of the growth from extending back to the

heater, to arrange a cooling pipe in front of the growing front and hence parallel to the narrow side of the plate-shaped carrier. Such a cooling tube, which is shown in the illustrated embodiment and denoted by 6, extends perpendicularly to the plane of illustration, along the narrow side 14 of the carrier 1 and is traversed, for example, by a cooling liquid. The cooling action produces a correspondingly intensive temperature gradient in the reaction gas mixture which promotes the dendritic growth. The heating device, for heating the narrow side 14 of the carrier, can be located outside the reaction space proper, in order to prevent precipitation of the semiconductor material at the heating device. This can be done, for example, by providing a reaction vessel with a window consisting for example of quartz and transparent or permeable only to the heat rays. Located inside the reaction vessel are the carrier 1 and, as the case may be, also the nozzles 8, 9 and the cooling tube 6. Whereas, the heater 7 is located outside of the reaction vessel, the heat waves acting upon the narrow side of the carrier only through the window. The nozzles and the cooling tube are vacuum-tightly sealed through the walls of the reaction vessel (not shown).

The thin plate-shaped semiconductor bodies produced by the method according to the invention will have the thickness desirable for electronic semiconductor devices and can be further processed by alloying or diffusion of doping substances into the plate surface planes, and by subdividing the semiconductor body, to thereby form the semiconductor elements used for example in the manufacture of transistors, diodes, solar cells and other electronic semiconductor devices.

By intermittent addition of doping substances such as boron, gallium, indium, aluminum, phosphorus, arsenic and antimony, particularly as gaseous compounds thereof to the reaction gas mixture, monocrystalline layers of respectively different doping, extending perpendicularly to the plane of the carrier plate, can be produced. This is of advantage for example in the manufacture of solid-state composite circuit devices such as multiple p-n junctions or assemblies of a plurality of semiconductor junction components. The addition of the doping substances may also be effected through the cooling-gas nozzles 8 and 9 for example.

The method of the invention can also be used in the production of monocrystalline, thin and plate-shaped semiconductor bodies of other semiconductor substances such as germanium or $A^{III}B^{V}$ semiconductors for example. In producing germanium semiconductors gas mixtures of hydrogen and any of $GeCl_4$, $GeHCl_3$, GeI_4 and GeH_4 may be used. In producing an $A^{III}B^{V}$ semiconductor, for example GaAs, mixtures such as $GaCl_3$, H_2 and As may be used.

Obviously, many modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

We claim:

1. A method of producing thin monocrystalline semiconductor bodies by thermal decomposition of a gaseous compound of the semiconductor substance and precipitation onto a carrier, which comprises placing a thin plate-shaped seed crystal, said seed crystal having a narrow edge, a broad surface and at least one twin plane extending parallel to its broad surface, into an atmosphere of a reaction mixture of the semiconductor substance, heating the narrow edge of said seed crystal to dissociation temperature of the reaction mixture while simultaneously cooling the reaction mixture in line with the twin plane of said narrow edge of said seed crystal between the heat source and said narrow edge, thereby producing a reaction zone at the narrow edge of said seed crystal causing semiconductor substance to precipitate on the narrow edge of said seed crystal, said seed being oriented so that said broad surface extends in the direction of the 111-plane and said narrow edge perpendicular to said broad surface extends in the 211-plane causing the rate of growth in the direction of the broad surface to be considerably greater than in the direction of said narrow edge, and pulling said seed out of said reaction zone at a rate corresponding to the semiconductor growth rate on the narrow edge.

2. A method for producing thin monocrystalline semiconductor bodies by thermal decomposition of a gaseous compound of the semiconductor substance and precipitation onto a carrier, which comprises placing a thin plate-shaped seed crystal having a narrow edge, a broad surface and at least one twin plane extending parallel to its broad surface, into an atmosphere of a reaction mixture of the semiconductor substance, heating the narrow edge of said seed crystal to dissociation temperature of the reaction mixture while simultaneously cooling the reaction mixture in line with the twin plane of said narrow edge of said seed crystal between the heat source and said narrow edge, rinsing the broad surfaces of said seed crystal with an inert cooling gas, thereby producing a reaction zone at the narrow edge of said seed crystal causing semiconductor substance to precipitate on the narrow edge of said seed crystal, said seed being oriented so that said broad surface extends in the direction of the 111-plane and said narrow edge perpendicular to said broad surface extends in the 211-plane causing the rate of growth in the direction of the broad surface to be considerably greater than in the direction of said narrow edge, and pulling said seed out of said reaction zone at a rate corresponding to the semiconductor growth rate on the narrow edge.

3. A method of producing thin monocrystalline semiconductor bodies by thermal decomposition of a gaseous compound of the semiconductor substance and precipitation onto a carrier, which comprises placing a thin plate-shaped seed crystal having a narrow edge, a broad surface and at least one twin plane extending parallel to its broad surface, into an atmosphere of a reaction mixture of the semiconductor substance and a doping substance, heating the narrow edge of said seed crystal to dissociation temperature of the reaction mixture while simultaneously cooling the reaction mixture in line with the twin plane of said narrow edge of said seed crystal between the heat source and said narrow edge, thereby producing a reaction zone at the narrow edge of said seed crystal causing doped semiconductor substance to precipitate on the narrow edge of said seed crystal, said seed being oriented so that said broad surface extends in the direction of the 111-plane and said narrow edge perpendicular to said broad surface extends in the 211-plane causing the rate of growth in the direction of the broad surface to be considerably greater than in the direction of said narrow edge, and pulling said seed out of said reaction zone at a rate corresponding to the doped semiconductor growth rate on the narrow edge.

4. A method of producing thin monocrystalline silicon semiconductor bodies by thermal decomposition of a gaseous compound of the semiconductor substance and precipitation onto a carrier, which comprises placing a thin plate-shaped silicon seed crystal having a narrow edge, a broad surface and at least one twin plane extending parallel to its broad surface, into an atmosphere of a reaction mixture of H_2, $SiHCl_3$ and a doping substance, heating the narrow edge of said seed crystal to dissociation temperature of the reaction mixture while simultaneously cooling the reaction mixture in line with the twin plane of said narrow edge of said seed crystal between the heat source and said narrow edge, thereby producing a reaction zone at the narrow edge of said seed crystal causing doped semiconductor silicon to precipitate on the narrow edge of said seed crystal, said seed being oriented so that said broad surface extends in the direction of the 111-plane and said narrow edge perpendicular

to said broad surface extends in the 211-plane causing the rate of growth in the direction of the broad surface to be considerably greater than in the direction of said narrow edge, and pulling said seed out of said reaction zone at a rate corresponding to the doped semiconductor silicon growth rate on the narrow edge.

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