



PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Production of Dislocation-free Single Crystals of Semiconductor Material

5 We, TEXAS INSTRUMENTS INCORPORATED, a Corporation organized according to the laws of the State of Delaware, United States of America, of 13500 North Central Expressway, Dallas, Texas, 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:—

10 This invention relates to a float zone process for forming single crystals of semiconductor material, in particular silicon single crystals, and more particularly to the control of a float zone crystal growth in which control is maintained over a molten zone and a freezing solid-liquid interface to minimise crystal dislocations.

20 In the manufacture of silicon semiconductor devices, high quality single crystals of silicon are necessary as starting materials. In accordance with one known method of growing crystals, a silicon seed is dipped into a molten pool of silicon contained in a quartz crucible and then slowly withdrawn. It has been found that resulting crystals contain approximately 10^{18} atoms per c.c. of oxygen which is derived from reaction of the molten silicon with the quartz crucible. This leads to undesirable heat treating effects as to the resistivity of the silicon body during subsequent processing. Thus, it is desirable to eliminate the high oxygen content.

35 In float zone processes of the type generally disclosed in U.S. Patent No. 2,992,311, a molten zone is caused to move along the length of an elongated silicon rod which is held in a vertical position. This method has the advantage of producing low oxygen content crystals, but has been found to be disadvantageous in that any crystal of reasonable diameter, such as above about one centimetre, contains a large number of dislocations. The

dislocations lower the minority carrier life-time and further act as preferential diffusion paths for impurities during further processing and for the foregoing reasons are highly undesirable. In a process disclosed by British Patent Specification No. 838770, contact between a molten zone and a single silicon crystal is established at the top pedestal of silicon which is longitudinally slotted. This slotting process and the fact that only small diameter crystals can be grown from the pedestal makes the system somewhat limited as a production operation although structurally perfect crystals may be obtained.

45 In accordance with one aspect of the present invention, there is provided a method of crucible-free formation of a dislocation-free single crystalline semiconductor material comprising the steps of forming a molten zone at one end of a semiconductor rod, attaching a seed crystal to said semiconductor rod at said molten zone, withdrawing said seed crystal a small distance to form a region of reduced cross-sectional area and passing said molten zone through the length of said semiconductor rod to form said dislocation-free single crystalline semiconductor material. Preferably the cross-sectional area from the region of reduced cross-sectional area to the rod progressively increases through a transition area to the rod diameter.

75 In practising the method, one boundary of the molten zone can be sharply defined by continuous liquid cooling of a single turn annular conductive member that is elongated in the axial direction of the rod and is so positioned in relation to a heating member, energisable to establish the said molten zone, to absorb power from the field produced by energisation of the heating member.

85 The invention also provides apparatus for crucible-free zone forming a rod of semiconductor material in which, in use of the appara-

centimetre

tus, a rod of semiconductor material is supported vertically at its lower end by a first support, and a single crystal seed of semiconductor material is supported by a second support disposed above the first support. The first and second supports are movable relatively towards and away from each other. The apparatus also includes a single turn, annular, inductive heating member for forming a molten zone in the said rod and, located beneath the heating member a single turn, annular conductive member which is elongated in the intended axial direction of the said rod and is so movable in that direction that it can be positioned to absorb power from the field produced by energisation of the heating member, and the elongated conductive member has defined therein a liquid coolant flow path. The cross-sectional area of the elongated conductive member can increase progressively away from the heating member and conveniently may be formed by a hollow truncated cone.

By way of example, the invention will be described in greater detail with reference to the accompanying drawings in which:

Fig. 1 is a diagrammatic view of an apparatus embodying the present invention;

Fig. 2 is a perspective view of the coil 13 and its support; and

Fig. 3 is an enlarged view of a seed and molten zone shortly after initiation of crystal growth.

Fig. 1 illustrates a system for float zone crystal growth in accordance with the present invention. A rotating single crystal seed 10 of silicon initially is dipped into a molten pool formed on the top of a rod 11 of silicon. Radio frequency power coupled to the silicon rod by a single-turn, closely-coupled coil 13 is adjusted until the tip of the seed melts, forming a continuous molten zone between the rod 11 and the seed 10. The seed 10 is then withdrawn from the melt, and the r.f. power and the withdrawal speed are so adjusted that a long neck 14 is formed below the seed 10. The neck 14 is of diameter smaller than that of the seed. After the neck 14 is of length of at least about one to two centimetres, the r.f. power and the seed withdrawal rate are then changed gradually to preset values, during which time a transition zone 15 is formed. Predetermined values of withdrawal and feed are reached which determine the diameter of the newly-formed crystal 17 above the melt zone 16.

Control is maintained over the heating zone and particularly over the geometry of the r.f. field sharply to limit the lower boundary of the field. This permits control over the molten zone thereby to assure a minimum occurrence of dislocations.

The system for carrying out crystal growth in accordance with the preferred embodiment of the invention is shown in Fig. 1. In this

embodiment, the lower end of rod 11 is supported in a chuck, which chuck is supported by a bottom mounting ring 20. The ring 20 is supported at the lower end of a rectangular frame 21 having two upper crossbars 22 and 23. The frame 21 is supported at opposite sides thereof on lead screws such as the screw 25 and by followers 26 and 27. The lead screw 25 is supported at its lower end by a member 30 of a fixed frame or support. A second lead screw (not shown) is similarly supported at its lower end and engages with the follower 26. A motor 31 is illustrated as connected to lead screw 25 by way of bevel gears 32. A similar driving arrangement is provided for the other lead screw. Preferably, the motor 31 will drive both lead screws so that the frame 21 may be precisely controlled in its movement upward relative to coil 13.

The seed 10, of rectangular cross section, is mounted in a chuck 35 and is solely supported in the chuck 35 as to be movable relative to the frame 21. The chuck 35 is supported at the lower end of a shaft 36 which is journaled in an upper housing member 37 and is provided with a drive pulley 38. The shaft 36 can be rotated by way of belt 39 driven from a motor 40 mounted on a cross plate 41 extending between a pair of followers 42 and 43 which are mounted on lead screws 44 and 45, respectively. The lower ends of the lead screws 44 and 45 are journaled in the crossbars 22 and 23. A pulley 46 is mounted on the lead screw member 44 between crossbars 22 and 23 and is coupled by way of a belt 47 to a first pulley on the shaft of a motor 48. In a similar manner, a pulley 49 mounted on the lower end of the lead screw 45 is coupled by way of a belt 50 to a second pulley on the shaft of the motor 48. Pulleys 46 and 49 are keyed to the lower ends of the lead screws 44 and 45, respectively, for transmission of driving forces thereto. As the motor 40 is energised, the shaft 36 carrying the chuck 35 is caused to rotate in order to rotate the seed 10. As the motor 48 is energised, the lead screws 44 and 45 are rotated, causing the followers 42 and 43 to be raised or lowered, depending upon the direction of rotation of the motor 48 so that the seed 10 may be raised or lowered relative to the upper end of the rod 11.

The housing 37 in which the shaft 36 is journaled is coupled by way of a flexible bellows 51 to the upper end of a mounting ring 52. The shaft 36 may be slidably supported in a bearing in the mounting ring 52. An auxiliary hand-powered drive arrangement is provided for raising and lowering the seed 10. A crank wheel 53 is coupled by bevel gears 54 to the shaft of motor 48 so that an adjustment can be made as to the elevation of the seed 10 without energising motor 48.

A quartz tube 60 is clamped in the rings 20 and 52 and is coaxial with the rod 11.

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Thus, all of the structure carried by frame 21 is movable relative to coil 13 so that a molten zone initiated in rod 11 may be caused to travel along the length of the rod 11 by raising the frame 21. Preferably, the travel of the frame 21 is carefully controlled as to be of constant speed so that mechanically induced aberrations can be avoided.

The character of the freezing interface between the melt zone 16 and the newly-formed crystal 17 and the starting rod 11 is maintained horizontal and flat by control of the molten zone. This is accomplished by control of the heating pattern from the coil 13 and by the movement of the newly-formed crystal 17 relative to the crystal 11. More particularly, the coil 13 is a hollow, single-turn copper loop such as shown in Fig. 2. It is mounted on a pair of brackets 70 and 71 which are insulated one from the other. The coil 13 is flow-connected at the ends of the single turn to a source of cooling water, the flow of which is maintained through the coil. The coil 13 is also connected to a source of r.f. power at frequency of about 4 megacycles and capacity of about 25 kilowatts. In addition to this, a focusing coil 72 is mounted immediately below the coil 13 and is in the form of a hollow, truncated cone having a centre bore through which the tube 60 extends. The focusing coil 72 is made of a highly conductive material such as copper and is provided with a pair of flow channels 73 and 74 leading thereto and which provide for flow of cooling water through the focusing coil 72. The coil is placed immediately adjacent to and immediately below the coil 13 and serves to rob power from the field produced by excitation of the coil 13; this serves to control the length of the molten zone and limits its shape. The control over the configuration of the freezing zone above the coil 13 has been found to be controllable by this means so that the crystal 17 may be grown above rod 11 of diameter equal to the diameter of rod 11 without the molten zone 16 falling out and with substantial freedom of dislocations.

A continuous flow of an inert gas, such as argon, is maintained through the tube 60 during the crystal growing cycle. Argon is introduced into the lower end of the tube 60 by way of a channel 75 and flows from the upper end of the system by way of a channel 76.

The growing cycle is initiated by playing a flame from a hydrogen torch 77 on to the wall of the tube 60 in a region preferably somewhat below the upper end of the rod 11. As the rod 11 is heated, the coil 13 is energised from a radio-frequency generator so that coil 13 becomes electromagnetically coupled to the rod 11. The coupling is such that the rod may be made molten by increasing the energy level of the field from coil 13. The flame from torch 77 is then turned off and

the rod 11 lowered so that the r.f. coupling zone is at the top of rod 11 at which point the r.f. power is increased.

As the rod 11 becomes molten, the seed 10 is lowered so that the lower end thereof is immersed in the molten pool on the upper end of the rod 11. Surface tension of the molten zone 16 and the electromagnetic field from the coil 13 maintains the integrity of the molten zone, preventing its falling out. The seed 10 is then rotated at a relatively slow speed and is slowly withdrawn from the upper surface of the molten pool on rod 11. The motors 31 and 48 are adjusted as to speed so that the crystal initially grown on to the seed 10 is necked down to a smaller diameter than the seed 10 and is permitted to maintain the relatively small diameter until it attains a length of several centimetres. At this time, the rate of movement of the seed 10 relative to the rod 11 is reduced gradually so that the transition zone 15 is formed. In operation, it has been found that the movement of the seed 10 relative to the rod 11 can be discontinued so that the newly-formed section 17 will have the same diameter as the original rod 11. The motor 31 then continues to drive the frame 21 upward, carrying with it the rod 11 as encased within the quartz tube 60. Thus, the molten zone 16 moves downward through the entire length of the rod 11 with the newly-formed crystal 17 freezing progressively above the molten zone as the body moves away from the zone controlled by the coil 13. A single pass beginning at the top of the rod 11 and terminating at the bottom of the crystal has been found to produce a crystal 17 which is free from dislocations and has a relatively low oxygen content and high minority carrier lifetime.

The traverse of the molten zone 16 down the length of the rod 11 may be of the order of about one hundred and fifty (150) millimetres per hour with no differential pull rate and with the rotation of the seed 10 and the newly-formed crystal 17 in the range of from about two (2) to twenty (20) r.p.m. The rotational speed preferably is in the lower end of the latter range. Crystals may be grown having diameters of two (2) to three (3) centimetres or more while maintaining the freedom from dislocations. The flow rate of gas by way of channels 75, 60 and 76, at a rate of about one-half litre per minute, has been found to be satisfactory. Higher flow rates are employed when the diameter of the newly-formed crystal section 17 reaches a diameter of about 3.3 millimetres. In the latter range, flow rates of one to 1.5 litres per minute will be employed.

In a typical example, the rod 11 may have a diameter of about twenty-eight (28) millimetres. The quartz tube 60 would have an inner diameter of thirty-two (32) millimetres and an outer diameter of thirty-four (34)



millimetres. The coil 13 is about five (5) millimetres tube size and of diameter such that the quartz tube 60 is free of the coil 13 but with minimum spacing therebetween. The focusing coil 72 is of the same inner diameter as the inner diameter of the coil 13 and the upper surface of the coil 72 was spaced about ten (10) millimetres below the lower surface of the coil 13. The coil 72 was of the order of one hundred and twenty-seven (127) millimetres in diameter at the bottom and slightly larger than the coil 13 at the top thereof.

In the foregoing example, the rod 11 was about twenty-eight (28) millimetres in diameter and the travel of the rod through the coil 13 was maintained at about one hundred and fifty (150) millimetres per hour. In instances where larger diameter crystals have been employed, such as thirty-three (33) millimetre crystals, the speed has been lowered somewhat to about one hundred and fifteen (115) millimetres per hour in order to assure a zone which is completely molten, and to avoid freezing up during the pulling operation. The traverse rate will thus depend upon the size of the rod employed and upon the power in the r.f. field. It should therefore be understood that the foregoing is given by way of example and not by way of limitation.

In order to form dislocation-free crystals, it is necessary that the seed 10 be thoroughly wetted in the molten zone on top of the rod 11 before beginning to pull the crystal. A guide by which the operation may be evaluated is illustrated in Fig. 3. The seed 10 is withdrawn from the molten top of rod 11 to form the neck 14 of reduced diameter to assure crystal structure of a large diameter which is dislocation-free. Crystal growth preferably is initiated when the lower end of seed 10 is of the shape illustrated in Fig. 3. More particularly, as the seed 10 rotates and becomes wetted in the melt, the corners of the seed tend to form cusps with downwardly pointed corners. When the seed 10 is shaped generally in the form indicated in Fig. 3, the pulling operation may then be commenced.

While not shown in the drawings, the system includes electrical controls for the speeds of motors 31, 40 and 48 as well as for control of the level of power from a suitable r.f. generator for the coil 13 of Figs. 1 and 2. Such controls are well-known in the art.

It is to be understood that the system operates to transfer semiconductor material from the bottom supported rod 11 into the form of a dislocation-free crystal. The operation is carried out in the argon atmosphere in the tube 60. The transfer, by way of a molten zone of controlled configuration, is on to a single crystal seed rotatably supported above the molten zone. The single-turn annular heating coil 13 encircles the rod 11 outside the tube 60 and is energised by high frequency

alternating current to create the molten zone in the rod 11. The single-turn, shorted focusing coil 72 encircles rod 11 immediately below the heating coil 13 to rob power from the r.f. field at the lower boundary to limit the height of the molten zone and thus control the molten zone.

The foregoing description has related primarily to the growth of crystal structures of silicon base materials. It will be recognised that other semiconductor materials may be similarly treated to produce dislocation-free structures. In the growth of germanium crystals, the primary problem attendant to the production of dislocation-free silicon crystals is not present. Thus, germanium can be grown from melts contained in quartz crucibles. Nevertheless, the present invention may be employed for production of germanium bodies which are dislocation-free, if desired. Since the density of germanium is somewhat greater than that of silicon, the diameter of the float zone would have to be maintained somewhat smaller in order to maintain its integrity.

In providing an inert atmosphere in which the molten zone is maintained, argon has been used and has been specified in the foregoing description. However, any inert gas which will not react with silicon at the temperatures involved would be suitable. Helium, neon, and the like, as well as hydrogen, are satisfactory.

WHAT WE CLAIM IS:—

1. A method of crucible-free forming of a dislocation-free single crystalline semiconductor material comprising the steps of forming a molten zone at one end of a semiconductor rod, attaching a seed crystal to said semiconductor rod at said molten zone, withdrawing said seed crystal a small distance to form a region of reduced cross-sectional area and passing said molten zone through the length of said semiconductor rod to form said dislocation-free single crystalline semiconductor material.

2. A method according to claim 1 in which there is formed a transition area of progressively increasing cross-sectional area between the said one end of the rod and the reduced cross-sectional area region.

3. A method according to either of the preceding claims in which following establishment of a molten zone at one end of the rod, a single crystal seed of semiconductor material is dipped into the molten zone and the seed is rotated while being withdrawn from the zone and the rod is moved upwardly through a heating member, the initial withdrawal rate of the seed being substantially in excess of the rate of upward movement of the rod and subsequently substantially corresponds with the rate of upward movement of the rod.

4. A method according to claim 3, in which withdrawal of the single crystal seed from the molten zone is commenced after formation of

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millimetres. The coil 13 is about five (5) millimetres tube size and of diameter such that the quartz tube 60 is free of the coil 13 but with minimum spacing therebetween.

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10 was of the order of one hundred and twenty-seven (127) millimetres in diameter at the bottom and slightly larger than the coil 13 at the top thereof.

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25 avoid freezing up during the pulling operation. The traverse rate will thus depend upon the size of the rod employed and upon the power in the r.f. field. It should therefore be understood that the foregoing is given by

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45 the seed tend to form cusps with downwardly pointed corners. When the seed 10 is shaped generally in the form indicated in Fig. 3, the pulling operation may then be commenced.

While not shown in the drawings, the system includes electrical controls for the speeds of motors 31, 40 and 48 as well as for control of the level of power from a suitable r.f. generator for the coil 13 of Figs. 1 and 2. Such controls are well-known in the art.

55 It is to be understood that the system operates to transfer semiconductor material from the bottom supported rod 11 into the form of a dislocation-free crystal. The operation is carried out in the argon atmosphere in the tube 60. The transfer, by way of a molten zone of controlled configuration, is on to a single crystal seed rotatably supported above the molten zone. The single-turn annular heating coil 13 encircles the rod 11 outside the

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alternating current to create the molten zone in the rod 11. The single-turn, shorted focusing coil 72 encircles rod 11 immediately below the heating coil 13 to rob power from the r.f. field at the lower boundary to limit the height of the molten zone and thus control the molten zone.

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In providing an inert atmosphere in which the molten zone is maintained, argon has been used and has been specified in the foregoing description. However, any inert gas which will not react with silicon at the temperatures involved would be suitable. Helium, neon, and the like, as well as hydrogen, are satisfactory.

WHAT WE CLAIM IS:—

1. A method of crucible-free forming of a dislocation-free single crystalline semiconductor material comprising the steps of forming a molten zone at one end of a semiconductor rod, attaching a seed crystal to said semiconductor rod at said molten zone, withdrawing said seed crystal a small distance to form a region of reduced cross-sectional area and passing said molten zone through the length of said semiconductor rod to form said dislocation-free single crystalline semiconductor material.

2. A method according to claim 1 in which there is formed a transition area of progressively increasing cross-sectional area between the said one end of the rod and the reduced cross-sectional area region.

3. A method according to either of the preceding claims in which following establishment of a molten zone at one end of the rod, a single crystal seed of semiconductor material is dipped into the molten zone and the seed is rotated while being withdrawn from the zone and the rod is moved upwardly through a heating member, the initial withdrawal rate of the seed being substantially in excess of the rate of upward movement of the rod and subsequently substantially corresponds with the rate of upward movement of the rod.

4. A method according to claim 3, in which withdrawal of the single crystal seed from the molten zone is commenced after formation of

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seed

- a wetting zone of very small cross-sectional area compared with the cross-sectional area of the rod.
- 5 5. A method according to claim 3, in which the single crystal seed has a polyhedral cross-section, and in which withdrawal of the seed from the molten zone is commenced after the development of downwardly extending peaks on the corners of the seed.
- 10 6. A method according to any one of the preceding claims, in which one boundary of the molten zone is sharply defined by continuous liquid cooling of a single turn annular conductive member that is elongated in the axial direction of the rod and is so positioned in relation to a heating member, energisable to establish the said molten zone, to absorb power from the field produced by energisation of the heating member.
- 15 7. A method according to claim 6, in which the cross-sectional area of the continuously cooled conductive member progressively increases in an axial direction opposite the direction of passage of the molten zone through the length of the semiconductor rod.
- 20 8. A method according to any one of the preceding claims in which the controlled atmosphere is provided by a continuously flowing inert gas.
- 25 9. A method according to claim 8, in which the inert gas is argon.
- 30 10. A method according to any one of the preceding claims, in which the semiconductor rod and the single crystal seed are a silicon rod and seed.
- 35 11. A method of crucible-free zone forming a rod of semiconductor material, substantially as described herein with reference to the accompanying drawings.
- 40 12. A dislocation-free crystal of semiconductor material prepared by a method as claimed in any one of the preceding claims.
13. Apparatus for crucible-free zone forming a rod of semiconductor material in which, in use of the apparatus, a rod of semiconductor material is supported vertically at its lower end, including a first support for supporting the rod at its lower end and a second support for a single crystal seed of semiconductor material disposed above the first support, the first and second supports being movable relatively towards and away from each other a single turn, annular, inductive heating member for forming a molten zone in the said rod, and, located beneath the heating member a single turn, annular conductive member which is elongated in the intended axial direction of the said rod and is so movable in that direction that it can be positioned to absorb power from the field produced by energisation of the heating member, and in which the elongated conductive member has defined therein a liquid coolant flow path.
- 45 14. Apparatus according to claim 13, in which the cross-sectional area of the elongated conductive member increases progressively away from the heating member.
- 50 15. Apparatus according to claim 14, in which the elongated conductive member is a hollow truncated cone.
- 55 16. Apparatus according to any one of claims 13—15, in which the elongated conductive member encircles a non-conductive tube that, in use of the apparatus, surrounds the said rod of semiconductor material.
- 60 17. Apparatus according to any one of claims 13—16, in which the heating member is hollow and defines a liquid coolant flow path.
- 65 18. Zone melting apparatus substantially as described herein with reference to and as illustrated by Figs. 1 and 2 of the accompanying drawings.
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