United States Patent

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[54] **METHOD OF PRODUCING SINGLE SEMICONDUCTOR CRYSTALS**
10 Claims, No Drawings

[52] **U.S. Cl.** ..... **23/301 SP,** 148/172, 252/62.3 E, 252/512
[51] **Int. Cl.** **B01j 17/00,** H011 7/40
[50] **Field of Search** ..... 252/512, 518, 521, 62.3 E; 23/301 SP; 148/171–173

[56] **References Cited**
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ABSTRACT: A method of making an ingot length of a single semiconductive crystal having substantially uniform resistivity throughout most of the length of the ingot is disclosed. An inert helium atmosphere is placed about a mass of silicon material and then the silicon mass is melted. A seed of silicon is inserted into the melt and withdrawn at a rate which provides a substantially uniform ingot diameter. As the seed is withdrawn from the melt, the pressure in the system is slowly reduced to vaporize the impurity from the melt so as to maintain a substantially constant impurity concentration in the melt during the formation of the ingot.

METHOD OF PRODUCING SINGLE SEMICONDUCTOR CRYSTALS

BACKGROUND OF THE INVENTION

This invention relates to a method of making a single semiconductor crystal and more particularly to a method of making an ingot of single semiconductive crystal having a uniform resistivity throughout a substantial portion of the length of the ingot.

In the manufacture of many semiconductor devices, it is desirable to obtain single crystals of semiconductor material which exhibit substantially uniform resistivity or conductivity throughout their lengths. Inasmuch as the resistivity is a function of certain active impurities present in the semiconductor crystal, this makes fabrication of single crystals having a substantially uniform impurity content highly desirable. The usual semiconductor materials are silicon and germanium, and the impurities most widely used are phosphorus, arsenic, aluminum, boron, gallium, indium and antimony.

In processing silicon or germanium for use in semiconductor crystal devices, it is usually necessary to melt and recrystallize the semiconductor in order to control its impurity content. In the Czochralski process, a widely used process for the commercial production of silicon, the semiconductor material is melted completely; after which, a seed crystal is brought into contact with the melt and slowly withdrawn, forming a single crystal by continuing accretion to the seed. In this growing method, the concentration of impurities in the recrystallized material tends to increase with continuing crystallization. As a result, the recrystallized material at the bottom of the ingot has a higher impurity concentration and the ingot does not exhibit the desired uniform resistivity or conductivity profile over its length. The typical resistivity profile of a silicon ingot containing phosphorus as an impurity obtained by the standard Czochralski process indicates about a 60 percent change in resistivity over 80 percent of the ingot. With a resistivity profile such as this showing such a large change in resistivity, the yield for a zener diode crystal doped with phosphorus, for example, is low—about 10 to 15 percent.

It is an object of this invention to provide a method of making ingot lengths of single semiconductor crystals having a substantially uniform resistivity throughout most of its length. It is another object of this invention to provide a method of making single semiconductor crystals in an ingot having a substantially uniform resistivity profile.

SUMMARY OF THE INVENTION

These and other objects of this invention are accomplished by a method in which a semiconductive material such as silicon containing a conductivity-type determining impurity is placed in a receptacle surrounded by an inert gas atmosphere, such as helium. The silicon mass is then heated to a temperature in the vicinity of 1,420° C. and melted. A seed of single crystal silicon is then inserted into the melted silicon and then withdrawn at a rate which provides a substantially uniform diameter for the single crystal ingot. In accordance with this invention, as the seed is withdrawn from the melt, the pressure of the inert gas atmosphere in the system about the melted silicon is slowly reduced so as to maintain a substantially constant impurity concentration in the melted silicon. After the single crystal ingot has been grown to the desired length, the ingot is cooled to room temperature. The resultant ingot has a substantially uniform impurity concentration throughout most of the length thereof. Since the impurity concentration is substantially uniform, the resistivity profile is also substantially uniform throughout most of the length thereof.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The invention will now be described in more detail. The semiconductive material employed is either silicon or germanium. Phosphorus, arsenic and antimony are the impurities most frequently used for the production of N-type silicon. Antimony and indium are the preferred impurities used with germanium in the practice of this invention. The concentration range of the impurity may vary over a broad range from a low of 1×10^{14} atoms/cc. (2 parts per billion) to 2.2×10^{19} atoms/cc. (1 million parts per billion) depending upon the desired resistivity of the resultant single crystal.

The semiconductive material, that is, the silicon or germanium, is placed in a crucible which is made of carbon in the case of germanium and quartz or glassy carbon in the case of silicon, as is the practice in the art.

An inert atmosphere is provided in the system by passing an inert gas, preferably helium or argon, over the silicon at a flow rate of 20 to 30 cubic feet per hour with a preferred flow rate being 25 cubic feet per hour. Other gases such as neon or xenon may be employed.

The semiconductive material is then melted. Silicon is heated to a temperature in the range of 1,420° C., whereas germanium is heated to a temperature in the vicinity of 946° C. After the semiconductive material mass has been melted, a seed of the same semiconductive material is inserted into the melted mass; for example, a silicon seed is inserted into the melted silicon.

As soon as a crystal commences to form about the seed, the seed crystal is slowly withdrawn at a rate such that a single crystal ingot having a relatively uniform diameter is obtained.

In accordance with the practice of this invention, a single crystal ingot having a substantially uniform resistivity profile over a major portion of its length is obtained by vaporizing the excess impurity from the melt as the seed or ingot is withdrawn thereby maintaining the impurity concentration of the melt at a substantially uniform level. In order to effectively maintain a substantially uniform or constant impurity concentration in the melt, it is necessary to gradually reduce the pressure in the system thereby vaporizing more impurity from the melt and preventing the concentration of the impurity in the melt from increasing.

The pressure in the system surrounding the semiconductive material mass is regulated by a series of vacuum pumps and by a valve attached to the inert gas source. The pressure of the system at the beginning of the process varies from about 50 to 760 mm. of Hg with the preferred pressure being around 100 mm. Hg. As soon as the withdrawal of the seed from the melt is started, the inert gas flow, preferably helium or argon, is gradually decreased by slowly closing or turning off the valve leading to the system from the inert gas supply. At the same time that the helium gas flow is being decreased, the vacuum system slowly reduces the pressure in the system. As the pressure is reduced, more of the impurity from the melt is vaporized thereby removing impurities from the melt which would normally increase impurity concentration level of the melt. By the proper programming or scheduling of the pressure reduction in the system, the impurity level in the molten mass or melt is maintained at a substantially uniform level. By maintaining the impurity concentration at a uniform level, the resultant resistivity of the semiconductor ingot is maintained at a uniform level thereby resulting in a uniform resistivity profile over about 80 to 90 percent of the length of the ingot.

The pressure is reduced from 50 mm. to 760 mm. Hg down to a level of from 10 mm. Hg to 1×10^{14} mm. Hg. The final pressure depends upon the resistivity desired in the ingot; that is, a pressure of the order of 1×10^{14} mm. Hg is used to obtain an ingot having a resistivity of 45 ohm centimeters, whereas a pressure of the order of 1 mm. Hg is used to obtain a resistivity of 0.005 ohm centimeters. The time required to reduce the pressure varies from ½ to 4½, the time required being less for ingots having higher resistivity. The pressure reduction can be carried out by the use of automatic instrumentation thereby lending itself readily to the commercial manufacturing of semiconductor ingots.

The complete growth cycle time of the ingot may vary from about 3 hours to 10 hours, depending to a large extent on the size of the silicon mass. Upon completion of the growing of the ingot, the ingot is then cooled and the pressure increased (example 1) to atmospheric pressure.

Silicon containing 3.6×10^{18} atoms/cc. of phosphorus was placed in the crucible. Helium, at a rate of 25 cubic feet per hour, was passed around the silicon mass. The silicon was heated to a temperature of about 1,420° C. and melted. A single crystal silicon seed was inserted into the melt and when the seed crystal began to grow, the seed was slowly withdrawn from the melt. The helium flow and the pressure in the system was slowly reduced over a period of 1.75 hours from 100 mm. Hg to 0.04 mm. Hg. The pressure was maintained at 0.04 mm. Hg for 3.75 hours to complete the growth of the ingot. The ingot was cooled and the pressure was increased to atmospheric pressure. The ingot had a tapered tip at both ends which was removed. Each tip amounted to 10 percent of the ingot length. The resistivity profile for the 80 percent of the ingot which remained after the top and bottom tapered portions of the ingot were removed was substantially uniform, the resistivity of the top end of the ingot being 0.0182 Ω cm. and the resistivity of the bottom end being 0.0180 Ω cm.

EXAMPLES 2 THROUGH 5

Ingot	P conc. in melt, atoms/cc.	Time, hours: Changing pressure	Time, hours: Constant pressure	Pressure, mm. Hg: Original	Pressure, mm. Hg: Final	Ingot resistivity,[a] Ω cm.: Top	Ingot resistivity,[a] Ω cm.: Bottom
2	2.6×10^{19}	2.0	3.5	100	1.0	.005	.0062
3	8.4×10^{17}	.75	4.75	100	.018	.041	.035
4	1.5×10^{17}	.5	5.0	100	.0001	.113	.100
5	2.26×10^{14}	.5	4.5	50	.0001	49.4	43.8

[a] 80% of ingot 4 and 5; 70% of ingot 2; 60% of ingot 3.

As can be seen from the examples, the resistivity varies to a relatively small extent from the top of the ingot to the bottom of the ingot when compared with the standard Czochralski process which is of the order of 60 percent change in resistivity over 80 percent of the phosphorous-doped silicon ingot. The method taught in accordance with this invention provides an economical way of increasing the yield of constant resistivity semiconductor crystal in an ingot.

We claim:

1. A method of making a single semiconductive crystal having a predetermined resistivity comprising the steps of:
   a. providing a mass of semiconductive material selected from the group consisting of germanium and silicon and containing a predetermined amount of conductivity-type determining impurity having a vapor pressure above that of said material,
   b. providing an inert gas atmosphere about said mass,
   c. melting said mass,
   d. inserting a seed of said mass material into said melted mass,
   e. withdrawing said seed at a rate such that the semiconductive material from the melt forms a single crystal propagated from said seed crystal,
   f. (reducing the pressure at a programmed rate of said inert gas atmosphere) during said withdrawing step, reducing the pressure of said inert gas atmosphere at a rate and to a value determined by said predetermined resistivity to maintain a substantially constant impurity concentration in said melted mass, and
   g. cooling said withdrawn material to yield a single crystal having a substantially uniform resistivity profile over a major portion of its length.

2. A method as described in claim 1 wherein said inert gas atmosphere is taken from the group consisting of helium and argon.

3. A method as described in claim 1 wherein said impurity is taken from the group consisting of phosphorus, arsenic, and antimony.

4. A method of making a single semiconductive crystal having a predetermined resistivity comprising the steps of:
   a. providing a mass of semiconductive material selected from the group consisting of germanium and silicon and containing conductivity-type impurity having a vapor pressure above that of said material,
   b. passing a gas taken from the group consisting of helium and argon about said mass at a flow rate of about 20 to 30 cubic feet per hour,
   c. melting said mass,
   d. inserting a seed of said mass material into said melted mass,
   e. withdrawing said seed at a rate such that the semiconductive material from the melt forms a single crystal propagated from said seed crystal,
   f. reducing the flow rate of said gas during said withdrawing step, and
   g. (reducing the pressure) during said withdrawing step, reducing the pressure of said inert gas atmosphere at a rate and to a value determined by said predetermined resistivity to maintain a substantially constant impurity concentration in said melted mass.

5. A method as described in claim 4 wherein said gas flow is reduced to less than 1 cubic foot per hour in 30 to 90 minutes.

6. A method as described in claim 4 wherein the pressure is reduced from between 50 to 760 mm. Hg to 1×10^{14} mm. Hg.

7. The method according to claim 1 wherein
   a. at the initiation of the withdrawing step, the inert gas atmosphere has a predetermined value and
   b. the rate of reduction of pressure of said inert atmosphere comprises a rate reduction from said predetermined pressure value to a lower value determined by said predetermined resistivity and a continuation of the said lower value of pressure during the remaining withdrawal of said crystal.

8. The method according to claim 4 wherein
   a. at the initiation of the withdrawing step, the inert gas atmosphere has a predetermined pressure value and
   b. the rate of reduction of pressure of said inert atmosphere comprises a rate reduction from said predetermined pressure value to a lower value determined by said predetermined resistivity and a continuation of said lower pressure value during the remaining withdrawal of said crystal.

9. The method according to claim 6 wherein the reduction in pressure is in two stages comprising
   a. a reduction from between 50 to 760 mm. Hg to between 1to 1×10^{14} mm. Hg during a portion of the crystal pulling process and
   b. a continuation of the pressure between 10 to 1×10^{14} mm. Hg throughout the remaining portion of the crystal withdrawal process.

10. The method according to claim 6 wherein the reduction of pressure from between 50 to 760 mm. Hg to about 1 mm. Hg is at a linear rate with respect to time and the reduction from about 1 mm. Hg to 1×10^{14} mm. Hg is exponential as determined by the needle valve construction being closed at a normal rate.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,615,261 Dated October 26, 1971

Inventor(s) Donald R. Causey, et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, lines 60 and 62, "10^{14}" should read -- 10^{-4} --,
Column 4, lines 36, 59, 61 and 67, "10^{14}" should read -- 10^{-4} --.

Signed and sealed this 10th day of October 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

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