May 14, 1957 R. E. DAVIS 2,792,317

METHOD OF PRODUCING MULTIPLE P-N JUNCTIONS

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Fig.1.

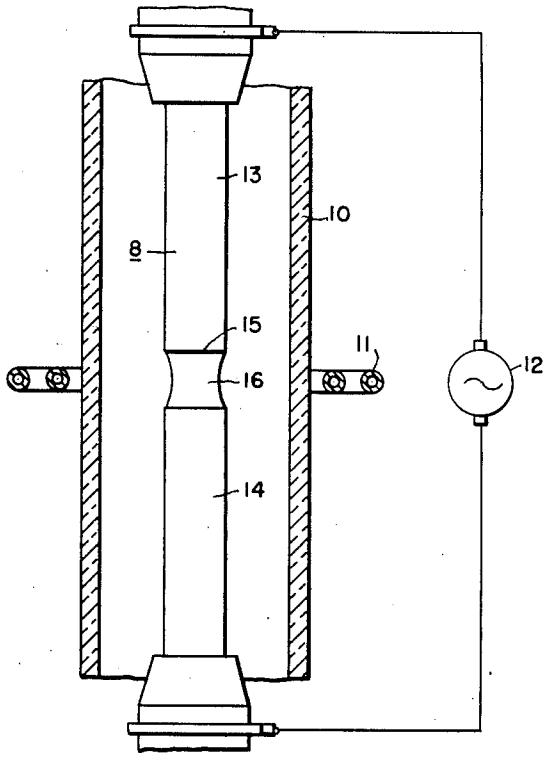
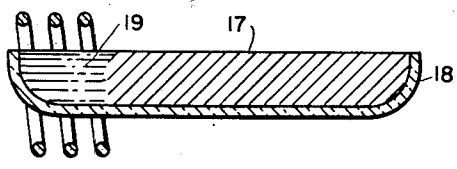


Fig.8.



WITNESSES

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Fig.2.

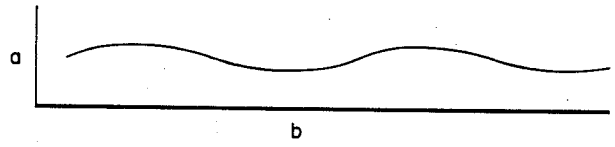


Fig.3.

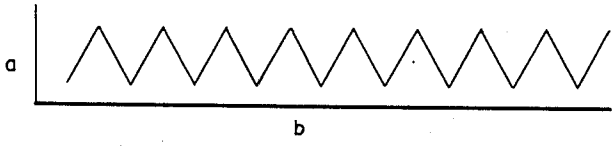


Fig.4.

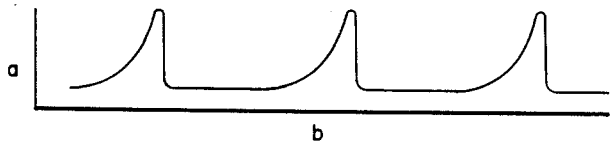


Fig.5.

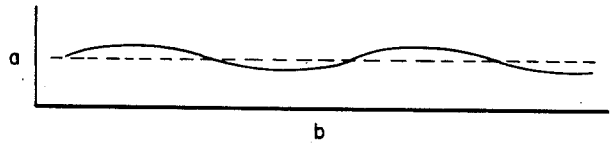


Fig.6.

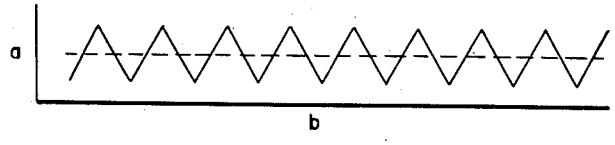
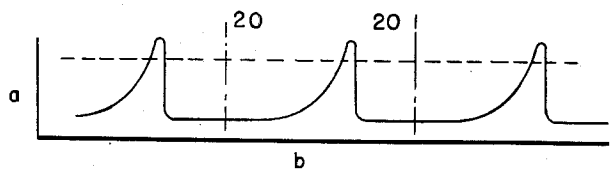


Fig.7.



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METHOD OF PRODUCING MULTIPLE P-N JUNCTIONS

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Application January 28, 1954, Serial No. 406,630

3 Claims. (Cl. 148—1.5)

This invention relates to a method of producing multiple P–N junctions in a single crystal of semiconductor material.

Certain intrinsic semi-conductors, such as germanium and silicon, can be converted into impurity semiconductors by "doping" them with minute amounts (less than 10 parts per million) of certain other elements, which are referred to as "impurities." When these intrinsic materials are doped with any impurity of the "P-type," such as indium, boron, aluminum, gallium, thallium, or copper, they are known in the transistor art as "P-type" material. When these intrinsic materials are doped with any impurity of the "N-type," such as arsenic, antimony, bismuth, or lithium, they are known as "N-type" material.

In the transistor and related arts it is sometimes desired to produce a "junction" between a body of one type material and a body of the other type material. Such a junction may be formed by alloying a body of P-type material to a body of N-type material. According to the present invention a single crystal of semi-conductor material is formed in such a way that along the length of the crystal the nature of the material changes from one type to the other, thus forming junctions.

For some purposes it is advantageous to produce a number of these P–N junctions in a single crystal. For example a crystal of this type is useful in photo-electric circuits, since the alternate regions of opposite conductivity-types will display a marked change in total resistance depending upon whether or not they are exposed to light. Also a crystal of this type may be cut into short sections, each section containing a P–N junction, and these sections can then be used in manufacturing transistors or other devices.

One method of producing multiple P–N junctions in a single crystal of semi-conductor material is disclosed in Patent No. 2,588,254. The method of that patent is, however, of limited use because it requires extensive facilities for the bombardment with charged particles, and because it is limited as to the patterns of varying concentrations of P and N type materials that can be produced.

The method of the present invention is an improvement over the method of that patent in that the present invention is not limited to the special bombardment apparatus, and can, therefore, be carried out with commercially available apparatus. Another advantage of the present method is that it can be used to produce varying patterns of impurity concentrations, thereby producing P–N junctions suitable for a wide variety of uses .

In general the present method consists of introducing into the crystal a first type of impurity which causes one type of conductivity, the strength of which varies for different zones of the crystal, and subjecting the crystal to treatment which introduces a substantially uniform level of conductivity of the opposite type, this uniform level being between the highest and lowest levels of the opposite type of conductivity. The planes where the

crystal changes from one type of conductivity to the other constitute P–N junctions. It is immaterial whether the constant-level of one type of conductivity is introduced first or last.

For a better understanding of the motive and objects of the invention, reference should be had to the following detailed description and drawing wherein:

Fig. 1 is a fragmentary cross-section view of a crystal melting apparatus;

Figs. 2 to 7 are graphs plotting concentration of impurities in a crystal at points along the crystal axis; and

Fig. 8 is a cross-sectional view of a refractory crucible containing a crystal.

These and other objects and advantages of the invention will become clear from the following explanation of several illustrative examples.

EXAMPLE I

A rod of silicon doped with indium to make it P-type material, is first passed through a zone-melting process so as to cause the concentration of indium to vary throughout the length of the rod.

This zone-melting step may be carried out in the apparatus illustrated in Fig. 1, in which a quartz tube **10** is surrounded by a pancake type of high-frequency heating coil **11**. A rod **8** of silicon is clamped at each end and moved upwardly through the quartz tube by suitable apparatus, and a current source **12** is connected to heat it whereby to bring the silicon conductivity into a range where the high frequency current generated at the zone **16** by the coil **11** can carry the heating up to the melting temperature of silicon. When the melting temperature is reached, the silicon rod **8** becomes molten in the heated zone **16**, this molten region being located between an upper solid portion **13** and a lower solid portion **14** of the rod **8**. As the rod **8** is moved upwardly the lower portion **14** passes progressively into the molten zone, and the upper portion **13** emerges from the molten zone, the freezing interface between the molten zone and the newly formed solid being indicated at **15**.

In order to stir the molten zone the upper rod **13** may be rotated rapidly, and the lower rod **14** may be rotated slowly in the opposite direction while maintaining alinement of the molten zone **16** with the upper rod **13**.

Changing the concentration of the first impurity

As previously explained, the rod **8** was originally doped with indium to form P-type material. Suitable steps are now taken to change the concentration of indium in different cross-sectional areas of the rod as it emerges from the molten zone. This can be done in any one of three ways:

1. *By changing the upward speed of the rod.*—The change of the upward speed varies the growth rate of the crystal, which in turn varies the amount of the impurity (in this case indium) picked up by the growing crystal.

As a typical example it may be assumed that the average rate of upward movement is 1 mil. per second. In this case the rate may be varied between 0.2 mil and 5 mil. per second, the slower rate producing areas of lower impurity concentration and the faster rate producing areas of higher impurity concentration.

2. *By changing the temperature.*—The growth rate can also be varied by changing the temperature of the melting zone. Raising the temperature of the molten zone decreases the growth rate for a short time, of the order of a few minutes per degree change, during which time the molten-zone length increases until a temperature gradient and growth rate nearly the same as before are obtained. This method would be used where the variations in concentrations are rapid enough that the diameter remains nearly constant, or where it is desired to "melt

back" to make a very abrupt change in concentration. An increase in temperature has the effect of decreasing the concentration of the impurity in the portion 13 at least until a new equilibrium is established.

3. *By changing the stirring rate.*—A change of the stirring rate causes a hydrodynamical change of the concentration of the impurity at the freezing interface 15, thereby changing the amount of the impurity picked up by the growing crystal. A faster stirring rate yields a lower concentration of the impurity in the freezing solid.

It should be understood that the impurity concentration of the rod may be changed by using only one of the above methods, or by using a combination of two or more of these methods.

Concentration patterns of the first impurity

Since each of the three ways of changing the amount of impurity picked up by the growing crystal depends upon the change of a rate, the rate of the change itself may be varied to produce different concentration patterns of the impurity along the longitudinal axis of the rod.

Thus if the rate of change is sinusoidal a curve representing the variations of impurity concentration in the resulting rod may be drawn as in Fig. 2, wherein axis "*a*" represents the concentration of the impurity and axis "*b*" represents the length of the rod.

A rate of change may be obtained which causes more abrupt variations in the impurity concentration as illustrated by the diagram in Fig. 3, where straight lines run from the points of high concentration to the points of low concentration.

Another type of rate change is illustrated in Fig. 4, where the line representing concentration curves up gradually to a peak and then falls off substantially vertically to a low point. This abrupt drop can be caused by use of the "melting back" technique, which is done by decreasing the growth rate to such an extent that the last-formed solid part of the bar is re-melted.

A wide variety of concentration patterns can be produced by this control of the growth rate.

Changing some areas to the opposite type of material

In the process as thus far described the rod of silicon is doped with indium so as to make it P-type, the indium being in different concentrations at different points along the length of the rod. Suitable steps are now taken to convert the areas of low indium concentration to the opposite type, or N-type of material. This may be done in different ways, as illustrated by the following examples:

1. *By diffusing an N-type impurity into the rod.*—According to this method an N-type impurity is diffused uniformly into the rod, as by diffusing lithium into the rod. This can be done by placing the rod in a vacuum chamber in the presence of lithium vapor and heating the rod to about 800° C. for a time enough for equilibrium stabilization. Under these circumstances the amount of lithium which diffuses into the rod depends primarily on the temperature, which can be accurately controlled.

The lithium may be readily uniformly distributed throughout the entire body of the rod in a sufficient concentration to convert the areas of low indium concentration to N-type, but not sufficient to change the areas of high indium concentration. This condition is illustrated in Fig. 5, where the dotted straight line represents the level of concentration of the N-type lithium, and the curved line represents the concentration of the P-type indium. (This curved line being the same as the curved line of Fig. 2.)

It is evident that where the curved line falls below the dotted line, the concentration of indium is lower than the concentration of lithium, and hence in the portions of the silicon rod represented by these areas, the lithium will predominate and these areas will have N-type characteristics.

Where the curved line extends above the dotted line, the concentration of indium is higher than the concentration of lithium, and hence in the portions of the silicon rod represented by these areas, the indium will predominate and these areas will have P-type characteristics.

The points where the curved line crosses the dotted line represents transverse planes across the silicon rod where the material changes from one type to the other, and the planes at these points are P–N junctions.

Fig. 6 illustrates the condition of a rod having the indium distribution of Fig. 3 after lithium has been diffused into it to the concentration indicated by the dotted straight line. It will be seen that with this sawtoothed curve for the indium the planes representing the P–N junctions cross the dotted line at more abrupt angles, and the junctions may be placed closer together.

Fig. 7 illustrates the addition of lithium to a rod having the indium distribution of Fig. 4. In this case relatively high and narrow peaks of indium concentration extend above the dotted line of the indium concentration. Because of the shape of these narrow peaks, the position of the dotted line is less critical, because slight variations in its level do not cause great changes in the location or slope of the points at the P–N junctions. This makes it easier to reproduce commercially junctions having substantially identical characteristics.

The actual curve shape used for the distribution of the first impurity will be determined by the use to be made of the junctions. Thus, a more gradual change as illustrated by the curve of Fig. 2 will produce a junction that will withstand a high voltage in the reverse direction. The junctions produced in a rod having the characteristics illustrated in Fig. 7 are particularly suited for use in transistors, because of the abrupt drop from a peak to a point of low concentration. These junctions may be separated from each other for use in transistors by sawing across the rod at the points indicated by the dot-dash lines 20 of Fig. 7.

2. *Other ways of changing to N-type material.*—Since the sole purpose of adding the lithium to the silicon bar is to produce in the bar a certain concentration level of N-type producing material, it will be understood that instead of introducing lithium, any other suitable method may be used that will change the material to N-type.

Thus the bar containing a given type of impurity at varying levels of concentration may be subjected to a long-term bombardment by charged particles, of the type disclosed in Patent No. 2,588,254 in order to create the opposite impurity at a desired uniform level.

Example II

In the example explained above the silicon bar was first treated to introduce a varying concentration of an impurity causing one type of conductivity, and was later treated to produce a substantially constant level of the opposite type of conductivity. It is possible to use the reverse of this procedure by first introducing a constant level of one type of conductivity and then introducing a varying level of the opposite type of conductivity.

One example of this second method may be carried out by first "doping" a silicon bar with boron to form P-type material, the boron being distributed at a substantially uniform level of concentration throughout the silicon bar.

A small slug of antimony (an N-type impurity) is placed near the starting end of the bar, and the bar is subjected to a zone melting operation as described above in connection with Fig. 1. It is possible to vary the concentration of the antimony by the same three methods mentioned above in connection with indium, namely,

1. By varying the speed of the rod.
2. By varying the temperature.
3. By varying the stirring rate.

During the process the concentration of antimony varies with the growth rate, because its *k* constant (the ratio of its concentration in the solid phase to its concen-

tration in the liquid phase) is much less than unity. However, the boron stays at substantially a constant concentration because its k constant is substantially unity.

Example III

In this example the starting material is germanium doped with antimony to form N-type material. A charge 17 of this material (see Fig. 3) is placed in a quartz boat 18 and is moved relative to a heating zone 19.

Suitable steps are taken during the zone melting to produce regions of different concentrations of the antimony. This may be done by changing the speed of relative movement of the heating zone and the charge, or by changing the temperature, or by changing the rate of stirring. The effect of these changes of conditions were explained above in connection with Example I. The result is a bar of N-type germanium with the concentration of the N-type impurity at different concentrations in different cross-sectional zones of the bar.

The bar is then subjected to a suitable treatment to convert to P-type the areas of low N-type concentration. This can be done by diffusing copper into the bar to a uniform level located intermediate the high and low levels of indium concentration. Copper is a P-type impurity and the level of concentration of copper must be high enough to change to P-type the areas which had a low concentration of antimony, the N-type impurity.

A quenching step may also be used to convert the germanium to P-type material up to the desired uniform level of concentration. This is done by heating the germanium to a temperature of somewhere between 500° and 950° C. and quenching it. The degree of conversion to P-type depends on the temperature to which the germanium is heated, and the speed of quenching.

Conclusion

It will be clear to those skilled in the art that this invention provides a simple and effective method of producing multiple P–N junctions in a single crystal of semiconductor material. It is possible to produce P–N junctions having different properties adapting them for different uses, and for application where it is desirable to have a large number of junctions in a short space, it is possible to produce as many as 50 P–N junctions per inch of bar.

According to the provisions of the patent statutes, I have explained the principle of my invention and have illustrated and described what I now consider to represent its best embodiment. However, I desire to have it understood that, the invention may be practiced otherwise than as specifically illustrated and described.

I claim as my invention:

1. In the method of preparing a body of semiconductor material with multiple P–N junctions, the semiconductor material being selected from the group consisting of silicon and germanium, the steps comprising introducing by zone melting at varying rates into the semiconductor body a first type of doping impurity at concentrations varying for successive zones of the body alternately above and below a given concentration level, thereafter diffusing into the body so doped a doping impurity of the opposite type, the latter impurity being distributed substantially uniformly throughout the body in a sufficient amount to equal the said given concentration level whereby at the zones where the first impurity exceeds the given concentration level the first type of conductivity will predominate while in the remaining zones the second type of impurity will predominate and the body at these other zones will have the opposite type of conductivity, whereby multiple P–N junctions result.

2. In the method of preparing a body of semiconductor material with multiple P–N junctions, the semiconductor material being selected from the group consisting of silicon and germanium, the steps comprising zone melting an elongated bar of the semiconductor material containing a first type of doping impurity so as to traverse the length of the bar by a relatively narrow molten zone, the concentration of the impurity in the solidified semiconductor material deposited from the molten zone varying with the growth rate of the semiconductor material from the molten zone, varying the growth rate to produce concentrations of the first doping impurity varying alternately above and below a given concentration level along the length of the bar, and thereafter diffusing into the bar a doping impurity of the opposite type, the latter doping impurity being distributed substantially uniformly throughout the bar in a sufficient amount to equal said given concentration level whereby at the points on the bar where the first doping impurity is above said concentration level the first doping impurity will predominate in the semiconductor at such points, while at the remaining points the second type of doping impurity will predominate.

3. The process of claim 2 wherein the semiconductor is silicon, the first doping impurity is indium and the diffused impurity is lithium.

References Cited in the file of this patent

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