July 8, 1958 R. W. LANDAUER ET AL 2,842,467

METHOD OF GROWING SEMI-CONDUCTORS

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FIG. 1

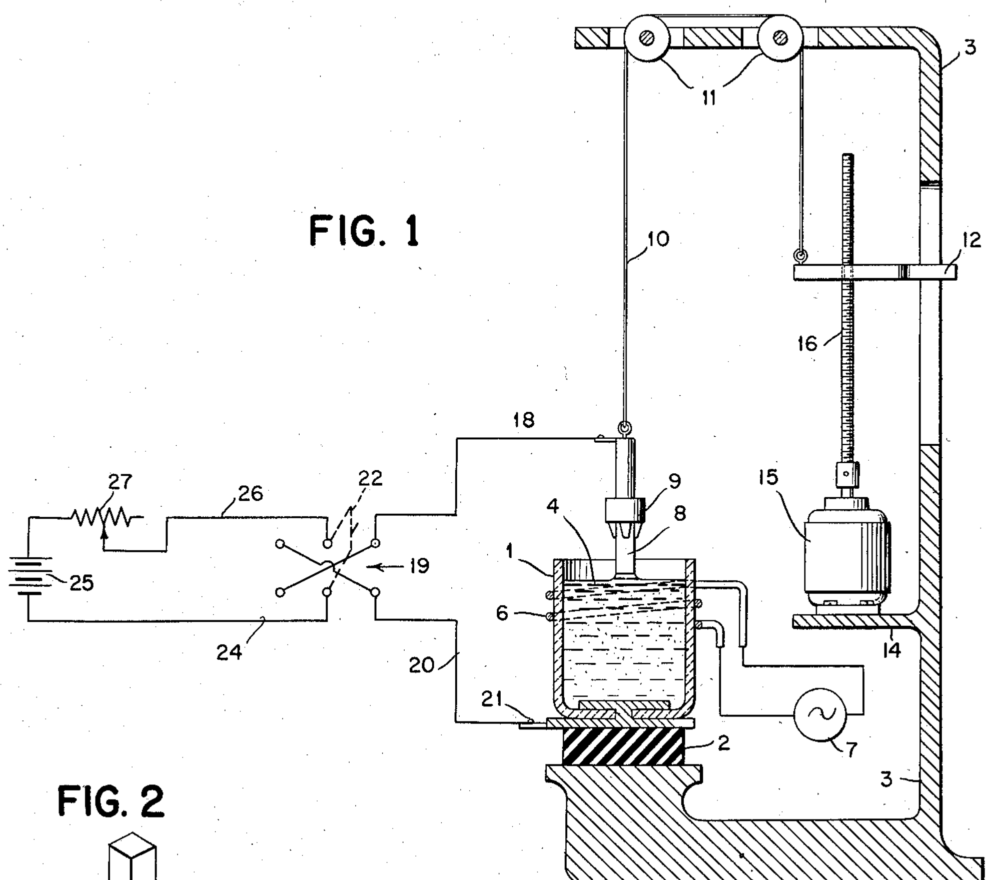


FIG. 2

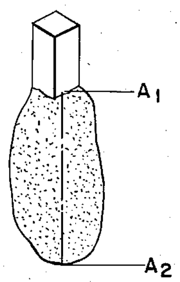


FIG. 3

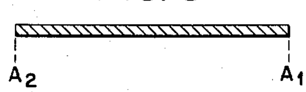


FIG. 4

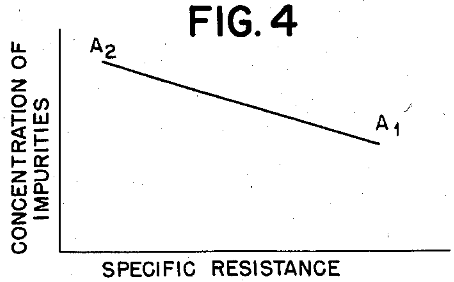
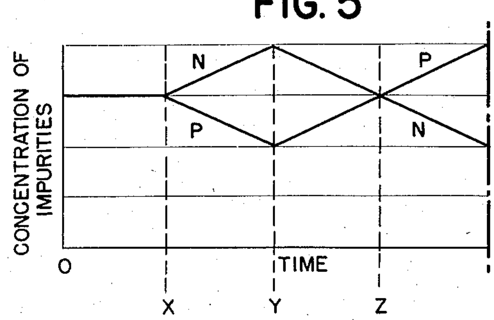


FIG. 5



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METHOD OF GROWING SEMI-CONDUCTORS

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4 Claims. (Cl. 148—1.6)

This invention relates to the fabrication of semi-conductor crystals, and more particularly to the control of the distribution of selected impurities added to semi-conductor crystals.

The semi-conductors used in rectifiers and transistors are made from a material of an extremely high degree of purity to which have been added very closely controlled quantities of selected impurities, and which has been grown into a single crystal. The concentration of these impurities in the crystal determines the desired electrical characteristics of the semi-conductor material. There are two basic types of these impurities, each imparting to the material certain unique electrical characteristics. The first type of impurity, comprising, preferably, elements of the fifth column of the Periodic Table which are Phosphorus, Arsenic, Antimony and Bismuth, is known as the "donor" type, and produces semi-conductor material known as "N" material. The second type of impurity, comprising, preferably, elements of the third column of the Periodic Table which are Boron, Aluminum, Gallium and Indium, is known as the "acceptor" type and produces semi-conductor material known as "P" material. An excess of one type of impurity over the other determines whether the material will exhibit "P" or "N" type unique characteristics, and the difference between the number of donors and acceptors present in a given quantity of semi-conductor material determines a general electrical characteristic, namely, specific resistance. Single semi-conductor crystals having alternate regions of "P" and "N" type material possess unique characteristics that are useful in transistor applications. The interface between the regions of "P" and "N" type material is known as a "P–N" junction. Another unique characteristic of semi-conductor material is known as the "Excess Carrier Lifetime" which is a measure of the speed with which the material will return to equilibrium when subjected to thermal or electrical excitation. The theories that have been advanced to explain these characteristics are well known and need not be discussed here. In the applications of semi-conductors, single crystals having various combinations of these characteristics are sometimes desired.

One method of growing a single crystal of semi-conductor material in use at the present time is performed as follows: A seed crystal of the semi-conductor material is immersed to a depth slightly below the surface of a quantity of molten semi-conductor material. This molten material is kept just a few degrees above its melting point while the seed crystal is withdrawn slowly, permitting the material of the melt to solidify on the face of the seed crystal. Semi-conductor material of the "P" or "N" type is formed by adding to the melt of pure material, amounts of P or N type impurity, as desired. Specific resistance is controlled by the quantity of impurity added in relation to the quantity of melt, and excess carrier lifetime is also controlled in this manner. The P–N junctions are formed by changing the predominance of one type of impurity over the other in the melt after a section of crystal of the initial type has been grown. This may be done in two ways, the first is to use a seed crystal of one type of material and grow a crystal from a melt of the other type of material, and the second is to add a quantity of one type of impurity, grow a length of crystal, and then add a greater quantity of the other type of impurity. The technology involved in the fabrication of this material is very complex and requires great skill. For example, impurity concentrations on the order of one impurity atom per ten millions of regular atoms can produce significant changes in the characteristics of the material, thus, the quantities of these impurities cannot be regulated by the usual chemical means. The degree of purity required of the semi-conductor material to be used as a crystal is greater than can be achieved by spectroscopic means. At the melting temperature, impurities can be absorbed from the atmosphere, hence these crystal growing operations are usually performed under controlled atmospheric conditions, or in a vacuum.

It is to the simplified and regulated control of the concentration of impurities in selected regions of the semi-conductor crystal that this invention is directed.

The primary object of this invention is to provide a close and simplified control over the distribution of impurities in semi-conductor crystals.

Another object of this invention is to provide a simplified method of forming P-N junctions in semi-conductor crystals.

Another related object is to provide a reliable and simplified method of controlling the specific resistance of semi-conductor crystals.

Still another related object is to provide a method of obtaining a semi-conductor crystal having a given excess carrier lifetime.

Other features of the invention will be pointed out in the following description and claims and illustrated in the accompanying drawings, which disclose, by way of example, the principle of the invention and the best mode which has been contemplated of applying that principle.

In the drawings:

Figure 1 is a schematic diagram of a system for performing the invention.

Figure 2 is an illustration of a semi-conductor crystal grown by the method used in this invention.

Figure 3 is an illustration of a segment of the crystal in Figure 2 cut lengthwise.

Figure 4 is a graphic representation of the variation of specific resistance with impurity concentration in a semi-conductor crystal and

Figure 5 is a graphic representation of the variation of impurity concentration with time in the presence of a varying electric field.

Referring now to the drawings and more particularly to Figure 1, a circuit is shown that may be used to carry out the invention. The circuit is connected to equipment used in one method of crystal growing which, in this instance, is used for illustration only, and the application of the invention should not be limited to this type of crystal growing operation because the specific invention the movement of impurities by an electric field may be applied in other ways to obtain a semi-conductor crystal.

The crystal growing equipment comprises a crucible 1 mounted upon an insulating block 2 carried by a supporting frame 3. Contained within the crucible is a semi-conducting material 4 comprising a metallic element such as germanium or selenium with closely controlled quantities of impurities for example those from either or both of the third and fifth columns of the periodic table, depending upon the electrical characteristics desired. This material is maintained in a melted condition by an induction coil 6 surrounding the crucible and connected to a suitable source of alternating current 7. A seed crystal 8 is supported by a holder 9 so that the lower end of the crystal engages the upper surface of the melted material 4, and the cable 10 is connected to the holder 9 and extends over pulleys 11 to a member 12 which is slidably mounted on the frame 3. Fixed to a flange 14 on the frame 3 is a motor 15 which drives a shaft 16 having threaded engagement with the member 12.

While the crystal 8 engages the surface of the material 4, a D. C. voltage is applied across them in one direction or the other. To accomplish this, a conductor 18 is connected from one terminal of a reversing switch 19 to the holder 9 which is made of conducting material and a conductor 20 is connected from another terminal of the switch to a contact member 21 engaging the material 4 at the bottom of the crucible. A reversible switch contact member 22 is connected by a conductor 24 to one side of a D. C. source 25 and is connected by a conductor 26 and a variable resistance 27 to the other side of the D. C. source.

In a crystal growing operation, the semi-conductor material 4 is kept in a melted condition by the heating coil 6. The seed crystal 8 is immersed in the melt 4 and then slowly lifted.

This is done by the motor 15 turning the threaded shaft 16 to draw the slidable member 12 downwardly and pull the cable 10 over pulleys 11 to raise the crystal holder 9 and the seed crystal 8. As the seed crystal 8 moves upwardly, the temperature of the melt at the lower end of the crystal drops and the semi-conductor material freezes on the end of the crystal. The speed of moving the seed crystal upwardly is a matter of technique, varied by many influencing conditions such as temperature and atmosphere, generally this speed is in the vicinity of .050 inch per second. The appearance of a crystal just after it has been grown is like that shown in Figure 2.

As the crystal is grown, the switch member 22 is closed in one direction or the other to apply an electric field across the seed crystal 8 and the melt 4. This field has the effect of moving the impurities and changing the distribution of impurities in the growing portion. It has been found that the distribution varies with the type of impurities in the melt and also with the intensity of the electric field. When the switch contact member 22 is moved to one of its closed positions and left there during the complete growing of a crystal, a segment (Figure 3) of this crystal, taken along the line A_1—A_2 in Figure 2 will exhibit a steady decrease in specific resistance with a corresponding increase in concentration of impurities as indicated in Figure 4. By determining the specific resistances of crystals grown with different types and amounts of impurities present, and with different voltages applied across the melt and the seed crystal during growing operations, it is possible to calibrate the system so that a crystal may be grown with any desired specific resistance. A crystal grown while impurities from the fifth column of the periodic table predominate will be of the "N" type, and that grown while impurities from the third column of the periodic table predominate will be "P" type. If impurities from both columns are present in the mix during the growing operation, the impurities from one column will predominate when the electric field is applied across the melt and the seed crystal in one direction, and those of the other column will predominate when the electric field is altered either in direction or intensity or both.

P–N junctions in semi-conductor crystals are produced by causing the concentration of one type of impurity, either P or N type to predominate while one section of a crystal is being grown and then causing the concentration of the other type of impurity to predominate over that of the first during the growing of another region of the crystal. This alternating predominance of one type

of impurity over the other may be accomplished by using the electric field to move the impurities and thereby produce an excess of the one type over the other in alternate regions of the crystal. The two types of impurities react to an electric field of a given polarity either by being influenced in the same direction at different speeds or by each type of impurity being influenced in opposite directions. The manner in which this reaction takes place has not definitely been established.

Referring now to Figure 5, curve N represents the concentration of N type of impurity and curve P represents the concentration of P type of impurity in the crystal. In this figure the curves are plotted to indicate movement in opposite directions of the two types of impurities in an electric field of a given polarity. This is done only to produce a clear picture and to aid in understanding and practicing the invention and should not be construed as a belief that this is the manner in which the impurity movement is influenced. It has been established only that a change in electric field will affect the spatial distribution of the impurities in the finished crystal.

In Figure 5, at time O the concentrations of both types of impurities are equal and curve N is superimposed on curve P. At time X an electric field is applied in one direction to produce a rate of change in the concentration of the impurities in the crystal and cause a concentration of one type of impurity, arbitrarily chosen as N, to exceed that of the other, resulting in a region of N type material being grown in the crystal. At time Y the polarity of the electric field is reversed to arrest the rate of change in concentration of the impurities in one direction and start it in the opposite direction. This is shown in Figure 5 by the fact that the concentrations of the two impurities represented by curves N and P begin to converge at time Y. The reversed electric field is continued until the concentration of the second impurity exceeds that of the first. This is shown in Figure 5 at the time following time Z, during which time a region of P type semi-conductor material is grown on the crystal. The point in Figure 5 where the two concentration curves cross is the P–N junction and is labelled time Z. This alternating of electric field polarity may be used to grow several P–N junctions in a single crystal.

This method of growing P–N junctions may be contrasted with the generally used methods in that in this method the impurities are added at the beginning of the growing operation and moved by the electric field to produce the desired predominance of impurities of one type over the other in the crystal; whereas, in the currently used methods the predominance of one type of impurity over the other is achieved by adding to the melt greater and greater amounts of the type of impurity necessary to change the type of material as the crystal is being grown.

Excess carrier lifetime in a semi-conductor is the rate at which the current carriers recombine in the crystal structure and depends in part on the impurity atoms present. It may be seen that a control of the distribution of the impurities in the crystal as it is grown will enable a control to be had over the carriers, and will result in permitting the growing of a crystal with a known excess carrier lifetime. A crystal of this type is grown in the same manner as a crystal having known specific resistance.

Whlie the method of controlling the distribution of the impurities in a semi-conductor crystal by the use of an electric field has been described for use as an independent method and has been contrasted with the currently used methods, this was done only to give a clear picture and not to imply that the method should be used separately. The method of the invention may be combined with any of the methods currently in use as may be expedient.

The reasons for the movement of the impurities by the electric field have not been definitely established, however, there are various theoretical reasons that may explain the phenomenon. These theoretical reasons are included merely as general information to assist in understanding and practicing the invention, and the movement of the impurities may be due to any one or any combination of these reasons or none of them.

One theory is that the impuriites may exist in the melt to some degree as ions which are free to move and which may be moved by the force exerted by the electric field.

Another theory is that the conduction electrons are accelerated by the field until they strike an impurity atom. When this collision occurs, the recoil imparts motion to the impurity atom.

Still another theory is that the distribution constant for the concentration of impurities existing in the melt is altered, to some degree, at the freezing interface and in the first few layers of atoms in the solid, by the electric field.

While there have been shown and described and pointed out the fundamental novel features of the invention as applied to a preferred embodiment, it will be understood that various omissions and subsitutions and changes in the form and details of the device illustrated and in its operation may be made by those skilled in the art without departing from the spirit of the invention. It is the intention therefore to be limited only as indicated by the scope of the following claims.

What is claimed is:

1. A method of growing a semi-conductor crystal comprising the steps of maintaining a pure elemental semi-conductor material with selected conductivity type determining impurities in a melted condition, supporting a seed crystal of the same material in engagement with the upper surface of said melt, applying a direct current electric field across said seed crystal and said melt, and lifting said seed crystal slowly to permit a freezing of the melt on the lower end of the crystal while said electric field is maintained.

2. A method of producing a semi-conductor crystal of varying specific resistance comprising the steps of immersing an elemental semi-conductor seed crystal in a melt of the same semi-conductor material containing selected conductivity type determining impurities, withdrawing said seed crystal slowly from said melt so that said material of said melt freezes on said crystal, and passing a direct electric current through the combination of said melt and said seed crystal during said withdrawing step.

3. A method of growing a semi-conductor crystal of predetermined specific resistance and given excess carrier lifetime, comprising the steps of immersing an elemental semi-conductor seed crystal in a melt of the same semi-conductor material containing selected conductivity type determining impurities, withdrawing said seed crystal slowly from said melt so that said material of said melt freezes on said crystal, and passing a direct electric current of selected intensity through the combination of said melt and said seed crystal during said withdrawing step.

4. A method of growing a semi-conductor crystal comprising the steps of applying heat to a region of a body of elemental semi-conductor material containing selected conductivity type determining impurities, for maintaining said region in a melted condition, progressively cooling said melted material from one end to effect a crystalization of the material, and applying a direct current electric field across the combination of said melted material and said crystalized material during said progressive cooling step.

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