

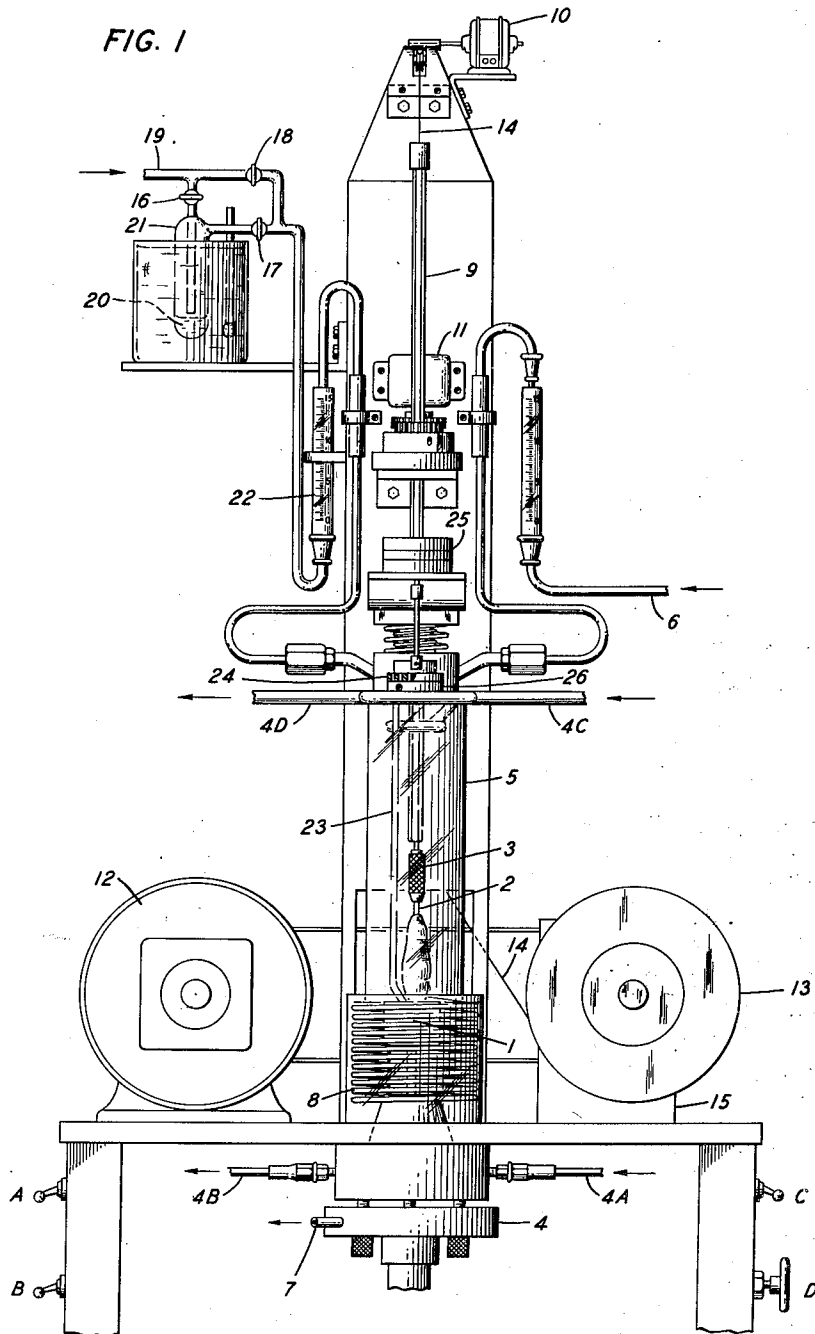
Oct. 30, 1956

E. BUEHLER ET AL
PROCESS FOR PRODUCING SEMICONDUCTIVE
CRYSTALS OF UNIFORM RESISTIVITY

2,768,914

Filed June 29, 1951

4 Sheets-Sheet 1



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FIG. 2

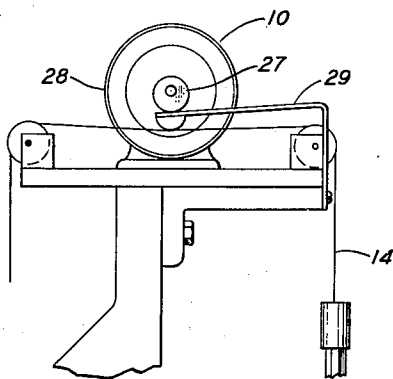


FIG. 3

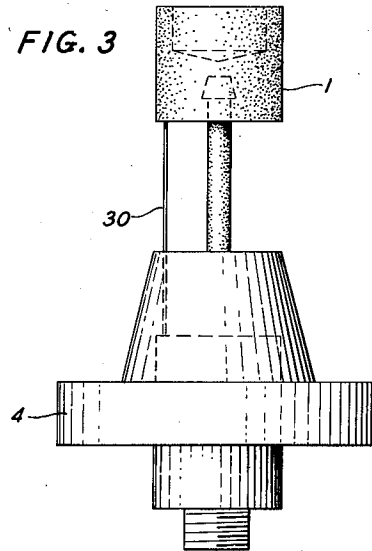


FIG. 4

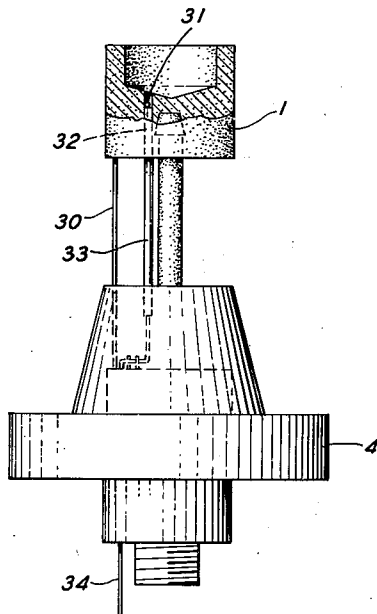
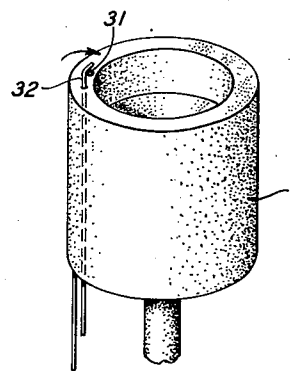


FIG. 5



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FIG. 6A

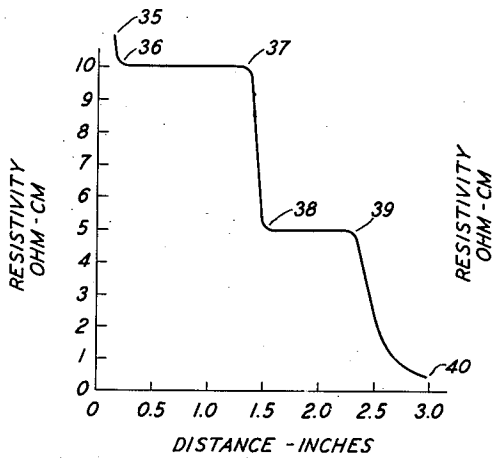


FIG. 6B

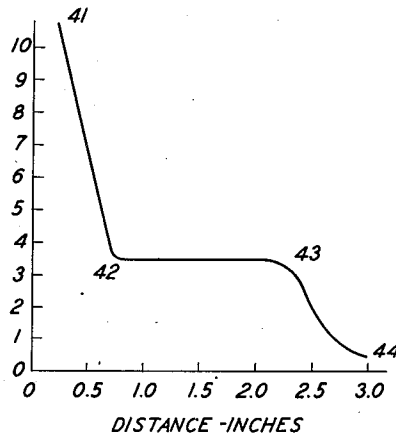


FIG. 7A

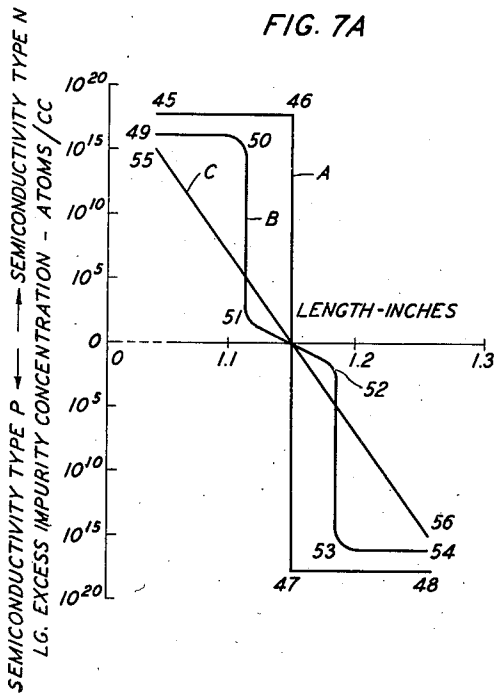
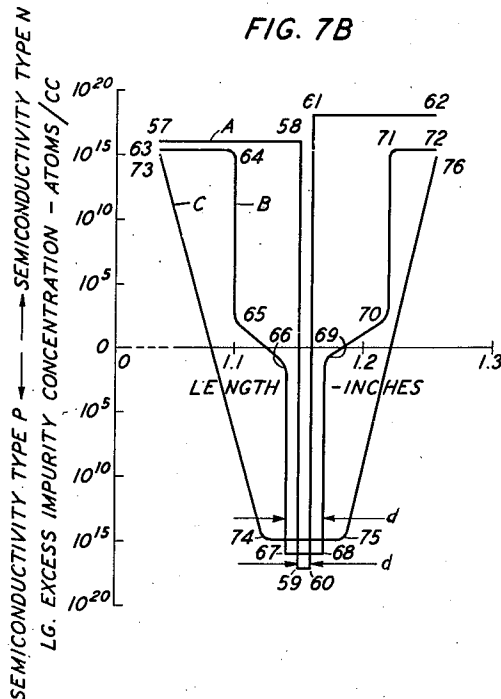


FIG. 7B



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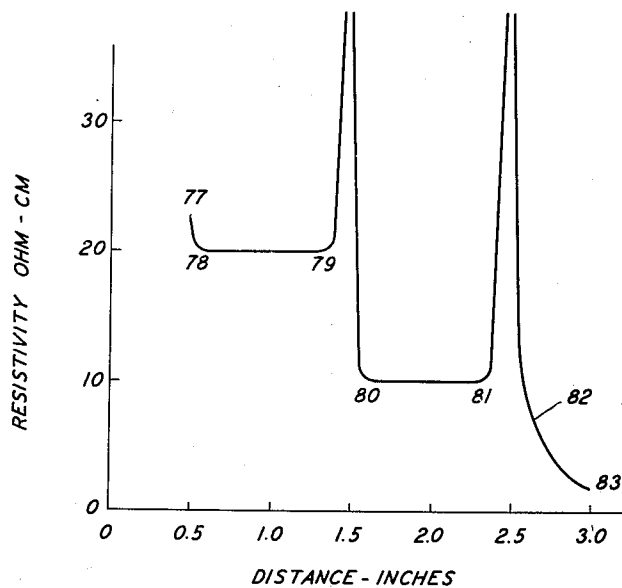
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FIG. 8



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2,768,914

PROCESS FOR PRODUCING SEMICONDUCTIVE CRYSTALS OF UNIFORM RESISTIVITY

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Application June 29, 1951, Serial No. 234,408

5 Claims. (Cl. 148—1.6)

This invention relates to methods of forming semiconductive materials usable, for example, in transistor and rectifier structures, and also to bodies of such materials so produced.

These semiconductive materials, of which germanium may be taken as an example, may be formed in rods of varying cross-sections, may be multicrystalline or may consist of but a single crystal, may be of constant resistivity and excess impurity concentration at any desired level over substantial portions of their length, may contain P-N boundaries at any desired location or locations longitudinally or laterally and of any desired electrical characteristics, and may contain N-P-N junctions at any desired location or locations, and of tailored electrical specifications.

In short, the process of the present invention consists of the drawing of a crystal or crystals from a molten body of a semiconductive material by dipping a seed crystal into the melt, allowing the interface of the crystal and the melt to arrive at thermal equilibrium and pulling the crystal at such a rate that the molten material crystallizes out on the seed. The forming crystalline body is rotated during the pulling procedure so as to result in a mass with a symmetrical cross-section and the pulling rate and melt temperature are constantly varied so as to control the level of excess impurity present at any point in the forming mass. Also described are means of controlling resistivity and conductivity type by additions of significant impurities and by heat treatment all during the drawing procedure.

It has previously been suggested that crystals of germanium could be grown from the melt using a constant pulling rate. It has been observed, however, that with a predominance of most significant impurities in germanium, resistivity in the solid decreases progressively in such a process as the molten mass crystallizes, thus indicating a Γ of less than 1 for these impurities (Γ =impurity concentration in the solid over impurity concentration in the liquid). That is to say, the forming crystalline matter approximates the normal freezing curve of the alloy of germanium and whatever impurity is being used. An example of such a freezing curve for antimony in germanium may be found in "The Physical Review," vol. 77, pages 809 to 813, March 15, 1950, Pearson, Struthers, Theuerer, Fig. 3.

By the process of the present invention, the normal freezing curve is avoided by varying the rate of pull. The general principle, where it is desired to produce a crystal having a constant resistivity zone and where Γ is less than 1 (as it is in all impurities thus far tested, for which Γ has been computed), is to decrease the rate of pull gradually as the crystal is formed so as to entrap less and less impurity and so as to negate the natural tendency of the forming crystal to follow its freezing curve.

Were rate of pull to be the only variable in the process, the crystal would increase in cross-section as drawn from the melt due to the dropping rate of pull. To counteract this effect and to maintain a constant cross-section over

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the constant resistivity zone, the decreasing pulling rates are balanced by an increasing melt temperature. The latter decreases the rate of crystallization and is monitored so as to be exactly equal and opposite in effect to the increase in cross-section that would result from the decreasing pulling rate.

The invention can be better understood by reference to the accompanying drawings in which:

Fig. 1 is a front elevation of a piece of apparatus on which the process of this invention can be carried out;

Fig. 2 is a sectional view of the vibrating member which beats against the wire supporting the crystal in the apparatus of Fig. 1, thereby having a stirring effect;

Fig. 3 is a front elevation of the crucible assembly embodied in the apparatus of Fig. 1;

Fig. 4 is a front elevation, partly in section, of an alternate form of crucible assembly showing doping means whereby the resistivity and conductivity type of the forming crystal may be influenced by the addition of controlled amounts of significant impurities;

Fig. 5 is a perspective view of still another form of crucible;

Figs. 6A and 6B are graphical representations of the variation of resistivity along the length of specimens which may be produced under different conditions of operation by the process of this invention;

Figs. 7A and 7B are graphical representations of the variation of impurity concentration along the length of specimens which may be produced under different conditions by the process of this invention;

Fig. 8 is a graphical representation of resistivity variation with length under still other conditions of operation.

Referring to Fig. 1, the apparatus is put into use as follows:

An ingot of the semiconductive material is placed in carbon crucible 1, a seed 2 of the same material is placed in chuck 3; crucible assembly 4 on which is mounted crucible 1 is then inserted in the bottom of quartz envelope 5. The equipment is flushed by passing nitrogen into gas inlet 6, through envelope 5 and gas outlet 7. After the system has been flushed with nitrogen, hydrogen or some other gas which will have a minimum effect on the composition of the forming crystal is then allowed to circulate by the same route and is continued throughout the process. A high frequency generator, not shown, is then turned on and a current is passed through induction coil 8 in order to heat carbon crucible 1. After the ingot is completely molten, spindle 9 to which seed 2 is attached is then lowered until the seed just touches the melt. Vibrator 10 and rotator 11 are then turned on. After the desired waiting period, motor 12 is turned on which in turn drives disc 13 which in turn and through cable 14 draws up spindle 9 thereby withdrawing seed 2 from the melt. The rate of draw may be controlled through gear box 15.

If what is desired is a single crystal of germanium, the process is allowed to proceed until all the melt has been withdrawn with appropriate variation in pulling rate and in temperature of the melt as later described. If it is desired to form a P-N boundary by gas doping at the appropriate point in the process, valves 16 and 17 are opened and valve 18 is closed thus allowing hydrogen to pass through inlet 19 through the reservoir containing the desired doping substance in liquid form 20 and gaseous form 21, thus sweeping doping gas 21 through flow meter 22 into atmosphere of quartz envelope 5. This doping gas could alternatively be passed directly into the melt through base 4, through a hole in the crucible, not shown, or through doping tube 23.

In certain cases it is desirable to dope by means of solid pellet. Where this is desired, the desired number and sequence of pellets may be mounted in magazine 24.

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At the desired time, motor 25 is turned on. This motor is directly coupled to dispenser 26 containing an opening which is brought in line with one chamber of magazine 24 thereby allowing a pellet to flow through tube 23 into the melt.

Throughout the process, cooling water is passed through water inlet 4A into a water jacket surrounding crucible 1 and is discharged through water outlet 4B. The upper portion of quartz tube 5 is also cooled by passing water through 4C and out 4D. Switches A, B, and C control, respectively, rotation, vibration and solid doping. Valve D controls gas inlet 6.

Fig. 2 is a detail drawing of vibrating member 10. Eccentric 27 mounted on the shaft of motor 28 causes shoe 29 to vibrate cable 14.

Fig. 3 is a detail view of the crucible assembly. From this figure, one may get a clearer picture of base 4 and crucible 1. The temperature induced in the melt and crucible 1 by coil 8 is controlled by means of an electrical circuit, not shown, monitored by thermocouple 30.

Fig. 4 illustrates an alternate crucible assembly construction to permit solid pellet doping. By this process the pellet 31 is placed in hole 32 and is supported by quartz rod 33 which can be raised above the surface of the bottom of the crucible by actuating steel rod 34. By this alternate process, pellet 31 is melted along with the melt in the crucible so that the doping material enters the melt not as a solid pellet but, rather, as a molten doping alloy.

Fig. 5 illustrates a crucible assembly for yet another alternate method of doping. By this process the pellet 31 is placed in an indentation on the rim of crucible 1. After this pellet has become molten and at the desired time, actuating member 32 which may be made of quartz or carbon is rotated so as to push the molten doping substance over the rim of the crucible 1 and into the melt.

Figs. 6A and 6B are plots of resistivity against distance measured by two point probes along single undoped crystals of germanium produced by this process. As may be seen from curve 6A, the resistivity of the initial portion of the crystal is dropped from point 35 to 36 while the cross-section of the crystal is allowed to build up. The portion of the curve between points 36 and 37 represents the desired constant resistivity zone which is produced by monitoring the drawing rate and the temperature as will be later described. After the drawing rate has come to a virtual standstill at point 37 so that no more crystal of resistivity 36—37 can be drawn, the resistivity is allowed to drop to a value represented by point 38 by a sudden increase in drawing rate. The drawing rate and temperatures are again monitored so as to result in flat portion 38—39. After the drawing rate has again come to a virtual standstill the rate of drawing is allowed to remain constant so as to draw up the remaining portion of the ingot resulting in normal freezing curve 39—40. Fig. 6B is similar to Fig. 6A but represents a crystal having only one flat resistivity zone. Increasing the pulling rate and decreasing the temperature to maintain the cross-section resulted in gradient 41—42. Zone 42—43 resulted from a normal monitoring of pulling and temperature rates as above described. Portion 43—44 represents the normal freezing curve in which the remainder of the ingot was drawn at any constant rate.

Figs. 7A and 7B are graphical representations of crystals which have been doped. The coordinates are log of excess impurity concentration expressed in atoms per cubic centimeter against length expressed in inches. The log of excess impurity concentration in the negative or downward direction represents a *p* conductivity type of decreasing resistivity, while the positive portion of the vertical represents *n* conductivity type. The resistivity values may be determined from the excess impurity concentration values by use of the equation

$$\rho = \frac{1}{ne\mu}$$

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where ρ represents resistivity in ohm-centimeters, n equals excess impurity concentration expressed in atoms per cubic centimeter, e is the charge on the electron, while μ is the mobility of the electrons or holes expressed in centimeters squared per volt second. Curve A of Fig. 7A represents the crystal which has been doped either with one large pellet or one burst of gas as later described. Zone 45—46 of this figure represents the constant resistivity section produced by monitoring the pulling rate and temperature. The pellet is dropped into the melt at point 46 resulting in sudden change in conductivity type 46—47 while section 47—48 represents that part of the crystal drawn from the remaining portion of the ingot. Although this portion of the curve appears to be flatter than the corresponding portions of Fig. 6A or Fig. 6B, both plotted in terms of resistivity against distance, it would appear similar to the normal freezing curve 39—40 if expressed on those coordinates.

Curve B in Fig. 7A represents a crystal with a P-N junction, produced by doping as in curve A except that by means of a controllable doping process using either multiple pellet or gradual gas doping the transition range is spread out from point 51 to point 52. Zone 49—50 again represents the constant resistivity portion produced by the normal monitoring process as will be described. The addition of a first pellet or burst of gas results in zone 50—51; zone 52—53 results from a similar addition of a pellet or burst of gas of opposite impurity type, while 53—54 is the normal freezing portion of the crystal resulting from drawing the remaining portion of the melt. Curve C of this same figure represents a crystal formed either through constant gas doping or multiple pellet doping resulting in a constant slope of curve 55—56.

Fig. 7B represents three illustrative crystals which have been doped during the drawing process so as to result in three different types of N-P-N junctions. Portion 57—58 of curve A represents the constant resistivity zone brought about as otherwise described, while 58—59 is produced by doping with a single pellet. Zone 60—61 represents doping with a pellet of opposite semiconductor type so as to bring the crystal back into the *n* region. Point 61 need not be higher than zone 57—58 but in this specimen the crystal was brought back to a higher *n* level at this point so as to produce a higher excess of *n*-type impurity which is desirable in a good emitter. Section 61—62 could again be a normal freezing portion of the crystal. The breadth *d* of the *p* region is determined by the time lapse between doping steps 58—59 and 60—61.

Curve B of Fig. 7B is similar to curve B of Fig. 7A except that after the crystal has been brought into the *p* region it is brought back into the *n* region by a reversed doping procedure using a pellet or gas of opposite semiconductor type. Therefore, section 63—64 represents the constant resistivity zone, while 64—65 represents doping with a first pellet or burst of gas. Section 65—66 represents controlled doping either with pellets or with controlled bursts of gas so as to produce the transition region. Section 66—67 represents doping with a large pellet or with a burst of gas. After an interval represented by *d* which may be controlled by varying pulling rate or time sequence the melt is doped with an impurity of opposite semiconductor type either by pellet or burst of gas to bring the crystal back to point 69. Point 69—70 represents controlled doping either by pellet or by a burst of gas. Point 70—71 represents doping in this example, of equal but opposite semiconductor type to that of zone 64—65, while 71—72 could again be normal freezing zone.

Curve C of Fig. 7B represents controlled gas doping or multiple pellet doping whereby the crystal is brought from point 73—74 either by constant gas doping or multiple pellet doping. Point 74—75 represents the region in which no impurity is added. This zone may or may not be of constant resistivity type as desired. Zone

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75—76 is the reverse of 73—74 and represents doping of an opposite semiconductivity type brought about either by gradual gas doping or multiple pellet doping.

Fig. 8 is a plot of resistivity against distance of a single crystal of germanium containing two constant resistivity zones 78—79 and 80—81 similar to those of the crystal of Fig. 6A but containing two N-P-N junctions 79—80 and 81—82 which were produced thermally and without the addition of any significant impurities by doping.

Although in theory, simply varying the pulling rates and varying the temperature as above described should result in a smooth, circular rod of controlled electrical characteristics, in fact, this was proved not to be the case due to a thermal gradient across the surface of the melt and consequent varying rates of crystallization on different portions of the forming rod. Not only were the surfaces of the forming rod caused to form in irregular fashion, but the electrical characteristics of the germanium were not kept constant even in cross-section. It was found that this could be overcome by rotating the crystal as it formed. Rotation rates of from 50 to 5,000 revolutions per minute are satisfactory and a rate of several hundred, as for instance 200 to 500, is to be preferred.

Although it was found that so rotating a crystal had sufficient stirring action to result in a rod of circular cross-section, at first glance, it was noted that ring-like irregularities were forming on the surface of the rod, especially at the lower speeds of rotation. This indicated that the temperature gradient, although diminished, was still in evidence.

It was found that this irregularity could be eliminated by the addition of a pumping action. This was done by adding a vibrating member placed in such a position so as to alternately stretch and contract the cable to which was connected the forming crystal. Vibration rates of from 10 beats per second at an amplitude of about 10 mils to about 500 beats per second at an amplitude of about $\frac{3}{4}$ of a mil have been found to be satisfactory, although here as with the stated rotation rates, the values cited are only suggestive and do not represent absolute limits. There is no apparent reason why they cannot be exceeded in either direction. Both rates are limited on the low side by ineffectiveness and on the high side primarily by equipment capability.

The crystals of the present invention may be formed from germanium ingots such as described in the copending application of J. H. Scaff and H. C. Theuerer, Serial No. 638,351, filed December 29, 1945, except that in order to minimize impurity content, the last portion of the ingot formed is cropped once and is remelted, re-frozen and recropped as often as is required depending on the purity desired. Varying this initial charge will, of course, vary the electrical characteristics of the final crystal.

Pulling rates of from .0001 up to .006 inch per second are habitually used. At rates higher than .006 inch per second, and, under some circumstances, even at this rate, a torsional strain results in the crystal causing twinning, which is generally considered undesirable in single crystals. For this reason, it is preferred not to exceed about .003 inch per second. The lower value represents only a practical limit. As will be seen from Example 9 below, it is sometimes desirable to reduce the rate of pull to a complete standstill.

As above set forth, when varying the pulling rate, it is necessary also to vary the temperature of the melt where it is desired to maintain the cross-sectional diameter of the forming rod constant. A typical schedule follows:

Pulling Rate, Inches Per Sec.	Temperature, °C.
.002	950
.001	965
.0001	980

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Although this monitoring may be done by hand, it has been found desirable to use an automatic programming control, several types of which are well known in the commercial chemical production field. Such a device is adjusted so as to vary pulling rates and temperature in accordance with the schedule above set forth. It should be noted that the tabulated temperatures represent measurements made at the wall of the crucible. Some time lag from the wall of the crucible to the melt is to be expected.

In order to maintain the lifetimes of the holes and conductivity electrons in the forming rod at the highest possible level, it is desirable to cool the rod as soon after it emerges as possible. This is done by means of water cooling coils and a constant flow of cooling gas through the envelope. Any good thermally conducting, non-oxidizing and otherwise non-reactive gas will be satisfactory for this purpose. Hydrogen, helium and nitrogen have been found to be satisfactory in this case.

One of the most important features of the process of this invention is the flexibility with which semiconductive transition zones may be produced. This may be done in two ways. The most important consists of doping either with a solid or with a gas containing the desired significant impurity in amount sufficient to carry the material over to the opposite semiconductivity type. Solid doping of crystals formed from charges of about 50 grams utilizes pellets of from 1 milligram up to 50 milligrams of alloys of germanium together with the desired impurity, or of any compound of the impurity which will have the effect of injecting the desired impurity into the melt.

The most satisfactory doping elements are gallium and boron for N to P conversion and arsenic and antimony where P to N conversion is desired. For solid doping the elements may be added in elemental form or in the form of any alloy or compound which will result in the addition of the impurity to the melt. Examples are the oxides and germanium alloys. The trichlorides have been found to be satisfactory in gas doping. Again the amounts of impurity used either in solid doping or in gas doping will vary with the size and purity of the initial charge, the amount of charge left in the crucible and the results desired. As has been seen, pellet doping may be carried out with the pellets in solid form or in molten form, and P-N or N-P-N junctions may be tailored to have any desired characteristics by varying in solid doping by the size of the pellets, composition of pellets, and time sequence of addition of said pellets; and in gas doping by the rate at which the gas is allowed to come in contact with the melt, and on whether or not it is passed in in bursts or gradually. With either type of doping, the junctions may be varied by controlling pulling rates and the temperature of the melt.

Another method of producing P-N and N-P-N junctions without addition of impurities is by the simultaneous variation of temperature and pulling rate. Here it is necessary to choose a starting material such that heat treatment at about 980° C. will produce a swing of semiconductivity type from N to P. An example of such a material is a germanium of a resistivity of at least 10 ohm-centimeters.

It may be noted here that a twin boundary may be formed either by using two seed crystals side by side, or by starting with a seed containing a twin boundary.

Where it is desired to produce a maximum amount of constant resistivity material, and after, through monitoring, the rate of pull has been reduced to a virtual standstill so as to make possible only a negligible increase in crystal length, it is possible to produce yet another constant resistivity zone in the same crystal. This zone will be, however, of lower resistivity. This is done by increasing the pulling rate to some maximum value suddenly and then monitoring its decrease as was done in the first zone. Since the normal freezing curve on co-

ordinates of resistivity against length is generally changing slope in this zone, it has been found preferable to decelerate the rate of pull more rapidly during the formation of this second portion of the crystal.

Although crystals may be grown using seeds of any crystalline orientation, it has been found preferable to either place the seed in such a position or to grind it in such a manner as to approximate the [100] or the [111] orientation.

A general description of a typical process for the production of a single crystal of germanium containing two constant resistivity zones follows: The seed crystal, cut from a rod produced by this process, is first cleaned and mounted in the chuck of the spindle. The charge, a one hundred gram germanium ingot such as produced by the process of copending application Serial No. 638,351, filed December 29, 1945, is loaded in the crucible, and the crucible assembly is mounted in position. The induction coil is turned on and the charge is melted at a temperature of about 980° C. The seed is immersed in a melt to a depth of about 5 mils and is left in this position sufficiently long to result in thermal equilibrium of the interface. A period of about five minutes has been found to be satisfactory. With the seed crystal being pulled from the melt at an initial rate of about .003 inch per second, the rotating mechanism is turned on and the vibrator is set into play. The temperature is dropped to about 935° C. and the pulling rate is kept constant for a period of three minutes. During this three-minute interval, the diameter of the crystal has increased to about 7/8 of an inch. Thereafter, where it is desirable to form a single crystal of uniform diameter, the rate of pull and the temperature are programmed as follows:

Pulling Rate Decreased to (Inches per Second)	Temperature Increased to (Degrees Centigrade)
.002.....	942
.001.....	970
.0001.....	980

The process thus far will result in approximately a 1½ inch constant-resistivity zone of about 10 ohm-centimeters. When the pulling rate has been reduced to a virtual standstill, the resistivity is dropped down to about half the level of the first zone by increasing the pulling rate to .003 inch per second suddenly. During the formation of this second zone, the pulling rates and temperatures are programmed exactly as above set forth, except at approximately double the deceleration rate. The rate of pull is then increased to any value and allowed to remain constant until the remainder of the melt has been drawn off.

If, at any time during the formation of the germanium crystal, it is desirable to form P-N or N-P-N boundaries, this may be done by pellet or gas doping by any one of the methods heretofore described. Typical examples of P-N and N-P-N boundaries that may be tailored to specification by varying pellet size and/or frequency, by varying gas doping rates, and/or by heat treatment, may be seen in Examples 3 through 9.

Examples of how the above processes may be modified to produce nine different types of crystals corresponding to the curves of Figs. 6A, 6B, 7A and 7B and 8 follow:

Example 1

The seed was mounted, the one hundred gram germanium charge was loaded and the crucible assembly mounted, as above set forth. After the charge had been melted, the controls turned on and the seed immersed in the melt to a depth of about 5 mils and allowed to remain in that position for about five minutes, the apparatus was set into motion. The initial pulling rate was .003 inch per second. The melt temperature was dropped

from an initial value of 980° C. to a value of about 935° C., the temperature change taking place in a period of about ten seconds. The pulling rate was maintained constant at the rate of about .003 inch per second for about three minutes during which time the diameter of the initial portion of the crystal increased to about 7/8 of an inch. The pulling rate and temperature were then programmed as set forth in the general description of the process above set forth. After the pulling rate had been reduced to a virtual standstill, the pulling rate was then increased suddenly to about .003 inch per second and once again the pulling rates and temperatures were programmed except at twice the deceleration rate. The remaining portion of the melt was then allowed to be drawn off at a rate of .003 inch per second. A crystal so produced is here referred to as a two-step crystal. This particular specimen contained two constant resistivity zones, one of about 10 ohm-centimeters running for a length of about an inch and a half, while the second zone had a resistivity of about 5 ohm-centimeters and extended for about ¾ of an inch. Where it is desirable to produce semiconductive material of constant resistivity, and where it is possible to use materials of both resistivity levels, it is this modification of the invention which produces the highest degree of efficiency.

Example 2

The crystal of Fig. 6B is a one-step crystal containing a sharp resistivity gradient and one constant resistivity zone. The process was set in motion as set forth in Example 1 and the crystal was allowed to build up at a rate of .0001 inch per second for a period of about five minutes. The drawing rate was then increased to about .003 inch per second, while decreasing the temperature in accordance with the following schedule:

Drawing Rate (Inches per Second)	Temperature (Degrees Centigrade)
.0001.....	980
.001.....	965
.002.....	950
.003.....	935

In the example shown in Fig. 6B, the pulling rate was varied as shown over a period of from two to three minutes. The pulling rates were then decreased and the temperature was then increased, as scheduled in Example 1. This monitoring sequence took about fifteen minutes and resulted in a constant resistivity zone of about 3½ ohm-centimeters over a length of about 1¾ inches. The remainder of the melt was then run off at any desired speed resulting in the normal freezing portion 43—44 of Fig. 6B. The rate of pulling used in this final portion has not been specified since to date this portion of the crystal has not found use in any transistor or rectifier device and is simply reused as part of the load of another run.

Example 3

The seed was mounted, the charge was loaded and the equipment was set into operation, as above described. The pulling rate was allowed to drop to about .0001 inch per second, while monitoring the temperature and pulling rates as above scheduled. The pulling rate was allowed to remain constant at this value for about seven or eight minutes and all the desired impurity was added at this point in the form of a pellet. In order to obtain a crystal of electrical characteristics such as indicated by curve A of Fig. 7A, a lump sum of impurity which would result in a total change in the crystal of about 10¹⁹ atoms per cubic centimeter was added. For an ingot of about 50 grams, this amounted to a pellet of approximately 10 milligrams of gallium dioxide. An equivalent amount of boron in the form of a germanium alloy could have been used. This could also have been done with one blast of a

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doping gas such as boron trichloride or gallium trichloride, containing approximately twice as much of the desired impurity, since only about half of the gas goes into solution with the melt. The pulling rate was then raised to about .001 inch per second and the remainder of the melt was drawn out. The materials produced by such a doping process are usable in voltage regulating devices due to their low back voltage.

Example 4

Multiple pellet doping or gradual gas doping was resorted to in order to obtain a crystal with characteristics corresponding to curve B of Fig. 7A. The process was put into operation exactly as set forth in Example 3, and after the pulling rate had been allowed to continue at .0001 inch per second for several minutes, one pellet consisting of about 2 milligrams of a gallium-germanium alloy containing about .35 percent gallium was dropped into the melt by any of the doping methods before described. This was done in order to bring the excess concentration of impurity to about 10^2 atoms per cubic centimeters. Three 2-milligram pellets of a gallium-germanium alloy containing about .05 percent gallium, spaced about one second apart, were dropped into the melt. Finally, a second 5-milligram pellet of gallium-germanium alloy, containing about 1.4 percent gallium, was dropped into the melt. The remainder of the melt was then drawn out at a constant rate of about .001 inch per second. It should be noted that the breadth and electrical characteristics, such as the back voltage of the P-N boundary so produced, may be tailored as desired by varying any one of the following: the size of the pellet, the composition of the pellet, the number of pellets used, the time sequence and the drawing rate. It is also possible to produce a crystal corresponding to this curve by using gas doping. The first doping step could be by means of a burst of about 10 cubic centimeters of hydrogen gas containing in the neighborhood of 5×10^{15} atoms per cubic centimeter of gallium trichloride or any other gas containing the desired impurity of sufficient vapor pressure. The second doping step would consist of passing into the melt a doping gas at a constant rate over about one minute and containing sufficient impurity such that the level of the forming crystal is varied a total of 5×10^4 atoms per cubic centimeter. In order to bring the curve down to its final resistivity level, another short burst of about 10 cubic centimeters of hydrogen containing about the same amount of impurity is allowed to come in contact with the melt. Crystals so produced contain excellent P-N junctions and may be tailored so as to meet the exacting specifications of any desired rectifier or transistor structure.

Example 5

In order to produce a crystal corresponding with curve C of Fig. 7A, the process was set into motion as above described, except that the initial pulling rate was .001 inch per second. The diameter of the crystal was built up to about $\frac{7}{8}$ of an inch by dropping the temperature to about 935°C . while the pulling rate was maintained constant for from seven to eight minutes. Hydrogen containing sufficient impurity to vary the excess impurity level of the forming crystal about 5×10^{31} atoms per cubic centimeter of the desirable impurity in any utilizable gaseous form was then added at a constant rate over a period of from three to four minutes always keeping the pulling rate constant at about .001 inch per second. The only requirement for the gaseous compound here used other than that it be of sufficient vapor pressure is that it should not be one which will impair the semiconductive properties of the crystal form and that it be non-corrosive to the apparatus used. As above set forth, the trichlorides of gallium, and boron are satisfactory. It is conceivable that such a crystal could be produced using a very large number of very small pellets, although as

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can be seen, the degree with which such a crystal would approximate the constant slope of the curve will depend on the number of crystals used. The materials as produced in this example find use in high back voltage rectifiers.

Example 6

Curve A of Fig. 7B represents a doping process similar to that of curve A of Fig. 7A, except that after the semiconductive type was brought into the *p* region a pellet containing donor impurity was added. Such a run follows. After the pulling rate was maintained constant at .0001 for several minutes, and again with a 50-gram starting charge, a 5-milligram pellet of a gallium-germanium alloy containing about 1.4 percent gallium was added to the melt. After a time lapse of from five to ten seconds, a 10-milligram pellet of arsenic trioxide or pure arsenic was added (the reason that an arsenic-germanium alloy was not used here is that the solubility of arsenic in germanium is so slight as would make the alloy pellet prohibitive in size). After the second doping step, the drawing rate of about .0001 inch per second was maintained for about eight minutes. After this period the drawing rate was increased to about .001 inch per second and the remainder of the melt was drawn out. Materials formed by this process have been successfully used in N-P-N transistor structures such as those described in patent application of W. Shockley, Serial No. 34,423, filed June 26, 1948. Varying the breadth of the key region represented by *d* on the curve will affect the frequency cut-off of the final transistor structure. The smaller *d*, the higher the frequency cut-off. The breadth of this region may be varied by varying the time interval between the two pellets and/or by varying the drawing rate. The specimen of curve A of Fig. 7B was brought to a higher resistivity level after the key region, since this specimen was to be used as a transistor and since this zone was to be used as an emitter. An increased number of excess impurity atoms are desirable in that zone of a transistor which is to be used as an emitter.

Example 7

The initial portion of the crystal represented by curve B of Fig. 7B was produced by the same doping amount and sequence as crystal represented by curve B of Fig. 7A. After the last doping step, however, the rate of pull was maintained constant at .0001 inch per second for about five minutes, whereupon the same doping steps were repeated in inverse order using donor rather than acceptor impurity. Such materials also find use in N-P-N transistor structures.

Example 8

The crystal represented by curve C of Fig. 7B was produced by constant gas doping or, alternately, multipellet doping at twice the rate and half the time used in Example 5. After a time lapse of about fifteen minutes, the same gradual doping process was repeated, using impurity of opposite semiconductive type.

Example 9

To form a crystal corresponding to the curve of Fig. 8, it was necessary to start with the initial portion of the drawn rod at a resistivity level of at least 10 ohm-centimeters and preferably at least 20 ohm-centimeters. After the process had been set into motion as described in Example 1, and after the first constant resistivity zone had been formed at a level of about 20 ohm-centimeters, the rate of pull was reduced to zero, while the temperature was maintained at about 980°C . for a period of several minutes, whereupon a second constant resistivity zone was formed exactly as in Example 1, the level of the second zone, in this instance, being in the neighborhood of 10 ohm-centimeters. The pulling was again stopped, and the temperature was allowed to remain constant at about 980°C . for several minutes, thereafter the remainder of the melt was drawn out at some constant rate.

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Zone 77—78 represents that portion of the crystal drawn at a constant rate of .003 inch per second, during which time the diameter was allowed to build up to some desired value (in this specimen $\frac{1}{8}$ of an inch). Zone 78—79 represents a constant resistivity zone produced by decreasing the rate of pull from .003 inch per second down to 0 inch per second, and a simultaneous increase of the temperature of the melt of from 935° C. to 980° C. Zone 79—80, which in this specimen was about $\frac{1}{10}$ of an inch in thickness, resulted from keeping that portion of the crystal in contact with the melt for a period of about five to ten minutes, resulting in thermal conversion from N to P type. Zone 80—81 represents a second constant resistivity zone formed in the same manner within the same monitoring limits used in the formation of the first constant resistivity zone but at double the deceleration rate. P-zone 81—82 was produced by a second thermal conversion in the same manner and for the same time as that used in zone 79—80, while 82—83 represents that portion of the crystal which followed its normal freezing curve, resulting from drawing out the remainder of the melt at a constant pull rate of .001 inch per second. Material containing such N-P-N transition zones is produced without the use of any doping mechanism. There is, of course, no reason why this thermal conversion step may not be combined with any one of the doping methods above described so as to give any desired flexibility in the formation of the N-P-N transition areas. Crystals produced by the thermal conversion process above outlined have electrical characteristics making them suitable for use in devices such as those disclosed in the application of W. Shockley, Serial No. 34,423, filed June 26, 1948, now abandoned.

Although most of the description is in terms of germanium it is to be understood that the described process works equally well with other semiconductive materials. Silicon, for example, has been used and the crystals produced from this material have been found to possess excellent properties.

What is claimed is:

1. The method of producing a crystal of normally solid semiconductive material containing a significant impurity

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having a Γ of less than 1 comprising inserting a seed into a melt of the said semiconductive material containing the said significant impurity, and withdrawing the said seed at a decreasing withdrawal rate such as to substantially compensate for the resulting increasing concentration of the said significant impurity in the melt and such as to produce a crystal manifesting substantially uniform resistivity over that portion of the crystal produced while decreasing the withdrawal rate, the rate of withdrawal being at all times such as to maintain a solid-liquid interface between the crystal and the melt, Γ being defined as the ratio of impurity concentration in the solid to the impurity concentration in the liquid with the two phases at equilibrium.

2. The process of claim 1 in which the temperature of the melt is progressively increased as the withdrawal rate is decreased in such manner as to maintain the cross-section of the crystal substantially constant.

3. The process of claim 1 in which the crystal is rotated during withdrawal.

4. The process of claim 3 in which the normally solid semiconductive material is germanium.

5. The process of claim 2 in which the normally solid semiconductive material is silicon.

References Cited in the file of this patent

UNITED STATES PATENTS

1,353,571	Dreibrodt	Sept. 21, 1920
1,531,784	Hazelett	Mar. 31, 1925
1,921,934	Lewis	Aug. 8, 1933
2,091,903	Baggett et al.	Aug. 31, 1937
2,188,771	Welch	Jan. 30, 1940
2,514,879	Lark-Horovitz et al.	July 11, 1950
2,530,110	Woodyard	Nov. 14, 1950
2,683,676	Little	July 13, 1954

FOREIGN PATENTS

706,858	Great Britain	Apr. 7, 1954
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OTHER REFERENCES

40	Journal of Applied Physics, vol. 6, 1935, pages 111-116.
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