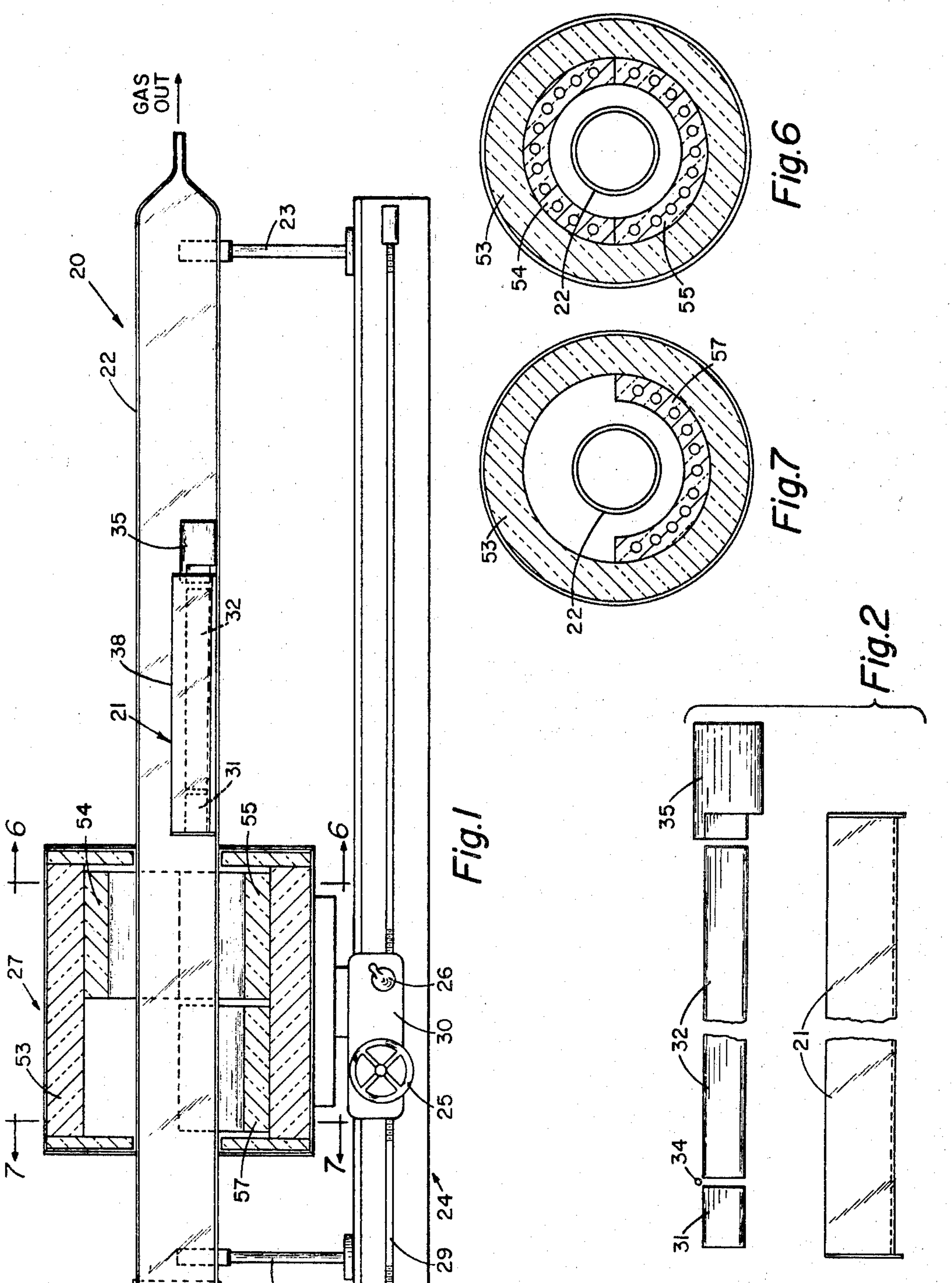
Sept. 10, 1968 W. B. MARSHALL ET AL 3,401,022
APPARATUS FOR HORIZONTAL ZONE REFINING OF
SEMICONDUCTIVE MATERIALS
Original Filed March 26, 1964 2 Sheets-Sheet 1



INVENTORS
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by Carol E. Marshall, Administratrix
and Howard W. Norman
BY Mueller, Aichele & Rauner
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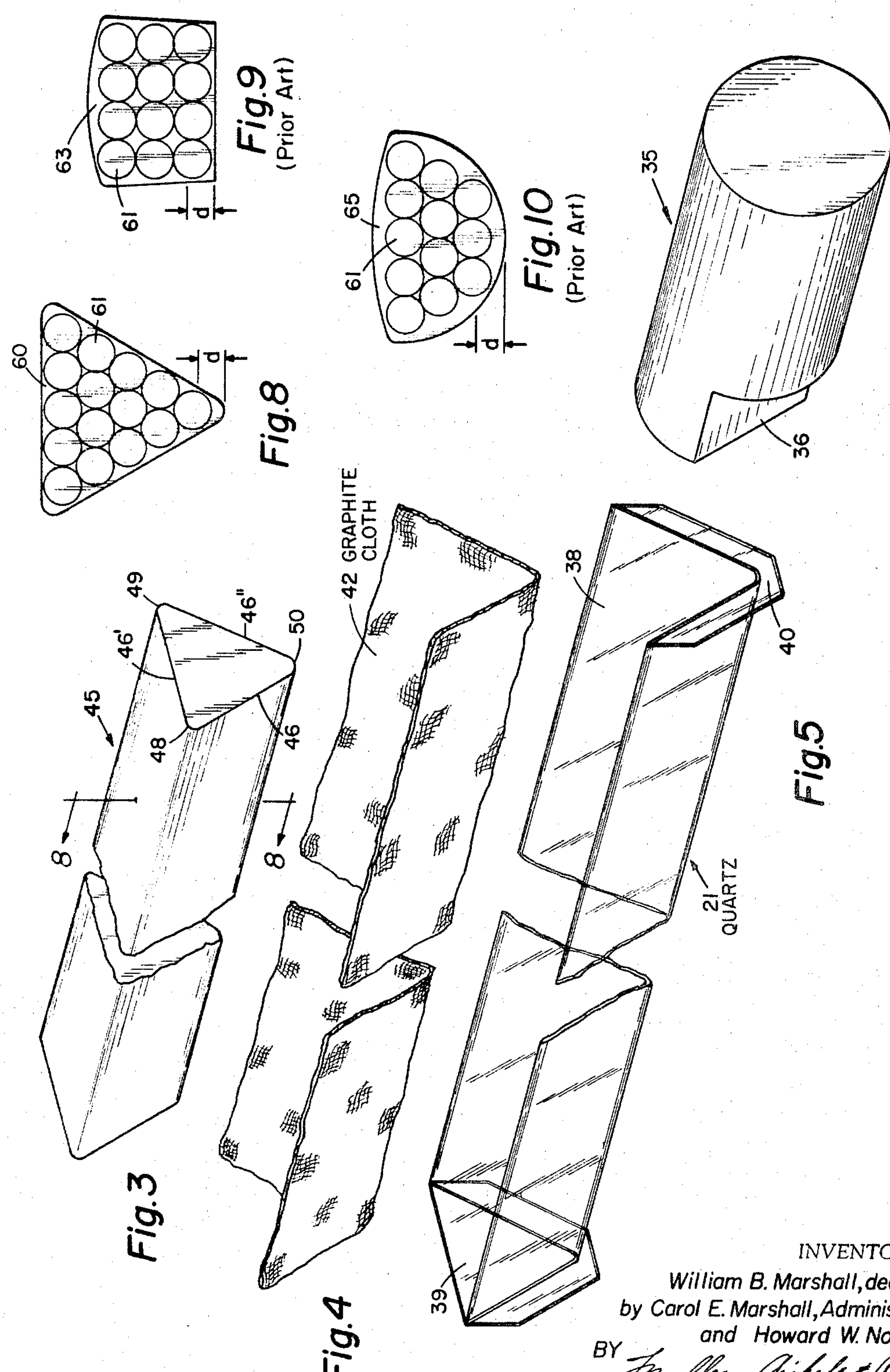

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APPARATUS FOR HORIZONTAL ZONE REFINING OF SEMICONDUCTIVE MATERIALS

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Original application Mar. 26, 1964, Ser. No. 356,007, now Patent No. 3,335,035. Divided and this application Mar. 13, 1967, Ser. No. 635,281
5 Claims. (Cl. 23—273)

ABSTRACT OF THE DISCLOSURE

Apparatus for zone refining semiconductive material, especially germanium, wherein a horizontal quartz boat has a liner of carbon fiber cloth for holding an ingot. The quartz boat preferably has an included angle of 60° for forming an equilateral triangular ingot. A carbon block at one end of the ingot serves as a heat conducting member to form a thermal continuation of the ingot for controlling temperature gradients therein.

This application is a division of our copending application S.N. 356,007 filed Mar. 26, 1964, now Patent Number 3,335,035.

This invention relates to a method and apparatus for growing monocrystalline germanium crystals, to the crystals grown by the same, and to the dice or crystal elements produced from crystal wafers cut or otherwise obtained from a grown-crystal.

So-called large area junctions in alloy-junction semiconductor devices present problems from cost and quality standpoints which start at the crystal growing stage and continue on through the cutting of dice and alloying of contacts thereon, right through to the complete fabrication of the semiconductor device and its operation. Many of these problems were solved by the Taylor invention of Patent No. 2,971,869 which issued Feb. 14, 1961, disclosing the fabrication of an alloy-junction semiconductor structure, and the structure itself, in which the semiconductor die or crystal element has a face or surface substantially parallel to any one of the structurally equivalent planes of the {111} group of Miller indices within the crystal element, and has an electrode alloyed to that face. Alloy junctions within such a crystal element contribute significantly to the uniformity of semiconductor structures made according to the invention of such patent, and to the excellency of operation of such structures. However, factors in the crystal itself, such as uniformity of resistivity in the grown crystal which in turn provides a uniformity in the many dice or crystal elements produced out of a grown-crystal, the lifetime of the elements, and other characteristics material to operation of semiconductor devices, called for improvement. Additionally, the yield of dice, or the number which could be obtained from a grown germanium crystal has been a very significant cost factor in the manufacture of alloy-junction devices. This made for an ever-present problem starting with crystal growing, and at this stage, the necessity for providing apparatus which would grow a crystal with top quality in each significant characteristic. Improvements made in initially growing a germanium crystal are actually reflected in the final cost of the structures or devices using the crystal material, and in the operation thereof in all of the many known applications for germanium alloy-junction devices.

An object of the present invention is to provide an apparatus and method for growing semiconductor crystals which is simple, and reliable, and produces a grown-crystal from which a greater number of dice or crystal elements per each grown crystal can be obtained than in the prior art, and with the same or improved operating characteristics in each element.

A feature of the present invention relative to the prior art is the provision of a horizontally disposed crystal-growing apparatus which includes an open boat or crucible that is triangular-shaped in cross-section to produce a corresponding cross-section in the grown-crystal, with the apex for the triangular cross-section at the bottom. During operation of the apparatus, the boat rests in a predetermined atmosphere in an enclosure, and a heater for the boat moves over the length thereof while the enclosure and boat remain stationary.

It has been the practice in the prior art with horizontally-placed receptacles in which semiconductor material is melted, to cover the inside walls of the receptacle with soot before placing crystal material therein. When the soot covering is not put on so as to fully cover the melting area, or is scratched or disturbed either during the loading of the receptacle or during the crystal growing opertion, serious damage can occur to the crystal being grown and a polycrystalline growth may result from the contact between the germanium and the quartz of the receptacle wall. It is a feature of this invention to provide a single piece of graphite cloth cut to a size to lay loosely over the inside wall of the receptacle to prevent any contact between the melted crystal material and receptacle wall so that a monocrystalline growth is accomplished. There is enough "give and take" in the cloth that it takes up expansion or contraction of the crystal during the entire growing operation.

A further feature of the invention is the production or the growing of a crystal having a triangular cross-section corresponding to the boat or receptacle in which it is grown, and such cross-section provides a greater number of dice or crystal elements of a predetermined size from each crystal wafer sliced or removed from the grown-crystal than has been obtained from wafers cut across any known prior grown semiconductor crystal of a corresponding bulk.

It is also a feature of this invention that the triangular cross-section of the crystal provides not only more dice or crystal elements for the same total bulk in the grown crystal relative to the grown semiconductor crystals in the prior art, but there is improvement in those characteristics of the semiconductor crystal elements which are important to the operation of the final semiconductor devices in which the elements are used.

Yet another feature of this invention is the orientation of the seed crystal so that as a single crystal of triangular cross-section is grown, crystal growth progresses from certain preferred planes identified by the Miller indices $(\bar{1}\bar{1}\bar{1})$, $(\bar{1}11)$, $(1\bar{1}1)$ and $(11\bar{1})$ as specially defined within this specification since it is easier to grow a single crystal from one of these planes, and moreover the crystal will be of a significantly high quality.

In the drawings:

FIG. 1 is a schematic-type showing of the complete apparatus of the present invention for growing a monocrystalline germanium crystal. A portion of the apparatus is shown in cross-section, and there are portions in dotted lines within the gas-filled enclosure in which the germanium is heated.

FIG. 2 is a developed illustration with a quartz boat or receptacle in a side elevation, and with the crystal material ready to be loaded in the boat for melting and for growing of a crystal.

FIG. 3 is a perspective view with a center portion broken away of the complete triangular cross-section grown-crystal.

FIG. 4 illustrates the piece of graphite cloth which is dropped into the quartz boat or receptacle of FIG. 5 to take the general configuration here shown when supported on the inside wall of the boat.

FIG. 5 is a quartz boat in perspective with the center portion broken away, and showing also a graphite plug (shown also in FIGS. 1 and 2) which is inserted in the open end of the boat when the germanium material is loaded therein for a crystal-growing operation. The graphite plug is independent of the boat itself.

FIG. 6 is a view along line 6—6 of FIG. 1, showing heating elements and the heater in cross-section.

FIG. 7 is a corresponding cross-sectional view along the line 7—7 of FIG. 1.

FIG. 8 is a cross-section through the line 8—8 of FIG. 3, and corresponding to the full size of a commercially grown germanium crystal according to the present invention, with the circles illustrating the position of dice or individual crystal elements to be made from a crystal wafer which in turn is cut out of or sliced at right angles across the crystal of FIG. 3.

FIG. 9 illustrates the cross-section of one configuration for germanium monocrystalline crystals grown according to prior art methods and apparatus, and illustrating the arrangement of round dice in a wafer of that cross-section. It shows directly the fewer number of elements which can be cut from a wafer of such a cross-sectional configuration.

FIG. 10 is another cross-sectional view illustrating the maximum number of round crystal elements which can be obtained from another wafer configuration cut or sliced from a crystal of corresponding cross-sectional configuration.

The illustration of FIG. 1 is more general than that of some of the other figures for different portions of the complete crystal growing apparatus **20**, and will be described in a general way, after which a detailed description will be made of those parts shown in detail in succeeding figures.

The quartz boat or receptacle **21** is positioned within a transparent hollow oven or chamber **22** in one commercial embodiment of the invention, and the oven is mounted stationary on supports **23** at each end. These supports in turn are mounted on the bed **24** of a lathe which includes a screw-driven carriage **30** upon which a furnace **27** is mounted. The screw **29** is motor-driven at a predetermined speed, and the carriage **30** is advanced longitudinally of the complete apparatus, as illustrated.

The crystal growing procedure begins with the loading of the quartz boat **21** in preparation for the charging of the crystal growing apparatus. In FIG. 2 is shown, in an exploded view, the crystal growing charge, which will be placed within the chamber **22** of the apparatus **20** prior to the crystal growing step. In making up the charge in the quartz boat **21**, the boat is lined with graphite cloth which is not visible in this view (but as shown in FIG. 4), and a germanium seed crystal **31** and an ingot **32** of nearly intrinsic zone refined monocrystalline germanium are placed on the liner in the boat. A small piece of strongly N or P type germanium **34** which is the source of impurity used to dope the crystal is likewise included in the charge, and a graphite plug **35** is provided to close the open end of the boat. The quartz boat **21**, graphite cloth liner **42** and graphite plug **35** are a part of the crystal growing apparatus **20**.

The quartz boat **21** is shown more clearly in FIG. 5. It consists of a V-shaped trough **38** having an included angle between the sides of 60°. Supporting members **39** and **40** of quartz are provided at each end of the trough **38** so that the boat **21** may be positioned properly in the chamber **22**, with supporting member **39** closing one end of the trough, while the other end of the trough is closed by the graphite plug or a block of graphite **35**.

The graphite plug **35** has three functions during the crystal growing procedure; it closes the end of the quartz boat **21** and thereby prevents molten germanium from flowing out of the boat, it serves as an expansion joint so that any increase in the overall length of the charge of germanium during crystal growth is accommodated without subjecting the germanium to appreciable strain, and finally, it acts thermally as a continuation of the germanium so that the heating and cooling characteristics of the germanium ingot will be substantially the same from one end to the other thereby insuring a more uniform final crystal. The graphite plug **35** is formed by machining one end of a round piece of nearly pure graphite (1 part impurity allowed in 10^5 parts graphite) so that it has a V-shaped portion **36** which accurately fits the open end of the quartz boat **21** when the graphite cloth liner is in place.

The seed crystal **31** and the ingot **32** are each triangular in cross-section. Each of the vertices of the triangular cross-section is approximately a 60° angle. Both the seed and the ingot have the same general shape as that of a finished germanium crystal **45**, an example of which is shown in FIG. 3.

In order that the finished crystal **45** may be cut perpendicularly to its length to form equilaterally triangular wafers whose major surfaces lie in one of the {111} planes, the seed crystal **31** used to start it growing in an acceptable orientation must be placed in the boat **21** adjacent the ingot **32** so that one of these planes is perpendicular to the sides of the boat **21**. Miller indices when shown enclosed by braces as in the preceding sentence, identify planes within a group which are equivalent though their specific indices may differ. For example, the group {111} includes the sets of equivalent planes with Miller indices (111), ($\bar{1}11$), ($1\bar{1}1$), ($11\bar{1}$), ($\bar{1}\bar{1}\bar{1}$), ($1\bar{1}\bar{1}$), ($\bar{1}1\bar{1}$) and ($\bar{1}\bar{1}1$).

In addition, to grow the best triangular crystals in this general {111} orientation with the least trouble, it is necessary that crystal growth occur in special or preferred orientations relative to the boat **21** as well as to the crystal and this requires extra attention to the placement of the seed crystal **31** in the boat. In order to discuss crystal growth relative to the boat **21** in a meaningful manner and subsequently to describe the preferred orientations of the seed crystal **31** relative to the boat, it is first necessary to define a set of references which uniquely relates the structure of the crystal to the shape of the quartz boat. This is most conveniently accomplished by choosing a set of parallel planes in the germanium crystal structure from the eight equivalent sets of planes with orientations according to the {111} group of Miller indices and then further defining that set of planes as being (111) planes or having the (111) orientation for just that position of the seed crystal relative to the boat so that when crystal growth from the seed occurs in an acceptable general orientation, i.e., so major surfaces of equilaterally triangular wafers cut from the crystal lie in one of the {111} planes, the part of the crystal where facets would ordinarily form will be on top of the crystal **46** and two sides **46′** and **46″** of the crystal that face against the two sides of the trough of the quartz boat **21**. Facets, in this case, are flat faces which are found on single crystals as a result of crystal formation rather than by cutting or shaping, or regions that would be flat faces had they not been constrained in some manner. When the position of the seed in the boat gives rise to crystal growth as described, the seed orientation relative to the boat (and of course the orientation of crystal grown from the seed) will be defined as being the (111) orientation. With the (111) orientation specially defined as above, it can be shown that the orientation of all other crystal planes relative to the boat are now uniquely determined, so one may now discuss directly the rotation of the seed into preferred or other orientations relative to the boat by the use of just the Miller indices alone. For example, if the seed crystal has a (111) orientation in the boat (as the (111) orientation has been defined with respect to the boat), the ($\bar{1}\bar{1}\bar{1}$) orientation is that which is achieved by simply turning the seed around so that the ends are reversed in the boat. Further rotation of the crystal from the ($\bar{1}\bar{1}\bar{1}$) orientation but about either the x, y or z crystallographic axis will produce the $(\bar{1}11)$, $(1\bar{1}1)$ or $(11\bar{1})$ orientations respectively.

There are four preferred {111} orientations relative to the boat, and it has been determined that for crystals grown in these orientations the quality is better and the incidence of twinning and the formation of polycrystalline crystals is less by more than 90% as compared to crystals grown on the other four orientations of the {111} group. The four preferred orientations are the $(\overline{111})$, $(\bar{1}11)$, $(1\bar{1}1)$ and the $(11\bar{1})$, and they differ from the (111) orientation as further defined in relation to the boat, in that crystal growth in one of these four orientations results in facets at the corner regions **48**, **49** and **50** of the crystal **45** (FIG. 3). While there is, of course, no difference in the true crystal planes of the {111} group, the orientations $(\bar{1}11)$, $(1\bar{1}1)$, $(1\bar{1}1)$ and $(\overline{111})$ as defined in relation to the boat are referred to as preferred orientations due to the fact that crystals grown in these orientations are superior and that there is a reduction in twinning and polycrystallization for crystal growth in these orientations. Twinning (i.e., the growth in a different orientation of a new crystal away from some plane of the crystal that was originally growing so that two different crystals exist on either side of the plane) as well as the formation of polycrystalline material readily originates at facets. Since there is much less area at the corners **48**, **49** and **50** of the crystal **45** than on the sides **46**, **46'** and **46"** of the crystal, it appears that the observed reduction in twinning in the commercial practice of the present invention, and the formation of polycrystalline material for growth from one of these four planes, may be explained by the probability that twinning and polycrystallization is less where the surfaec at which faceting occurs is small simply because there are fewer places at a smaller surface for twinning and polycrystallization to begin.

The graphite cloth liner **42** of FIG. 4 for the quartz boat **21** is a very flexible material and, when properly placed, it will rest smoothly against the sides of the quartz boat **21** in order that ingot **32** and seed **31** closely fit the V-shaped trough **38**.

The use of a graphite cloth boat liner **42** is especially important to the crystal growing procedure for several reasons. As is known, during the cooling and recrystallization of the germanium, if the germanium comes in contact with the quartz, the contact often results in the formation of twinned or polycrystalline germanium. In the past, quartz boats have been coated with carbon by smoking them in a flame such as the candle flame and by other methods, to provide a carbon or soot film in order to prevent contact between the quartz and the germanium. The soot film also prevents sticking of the germanium to the quartz. A soot film, however, is fragile and easily destroyed by the hard surface of the germanium, and unless considerable care is exercised during the loading of the quartz boat, the surfaces of the germanium will scratch away parts of the film and expose the regions of the underlying quartz. Even when these regions are extremely small they can still cause polycrystallization and twinning. However, when graphite cloth is used as a boat liner **42**, the germanium may be loaded into the boat **21** without any particular care, for the graphite cloth liner **42** is strong and is not damaged by loading procedures which would have ruined a soot film.

While the graphite cloth **42** does not provide a continuous or completely closed surface against the germanium, it is a fairly close weave, and since graphite is not wet by germanium the molten germanium does not flow through it and come in contact with the quartz.

The graphite cloth, of the particular type being used for this purpose, is fairly thick and is considerably freer of those impurities which degrade semiconductor material than is quartz. Furthermore, the cloth **42** has body and does not fit tightly against the side walls of the boat **21** as was the case for the soot film, and these conditions separate the germanium from the quartz in a way such that a reduction in amount of contamination of the germanium by impurity materials diffusing from the quartz, has been observed and contaminants in by the soot layer itself are not found in the graphite cloth.

Graphite cloth may be obtained from manufacturers having a total impurity content of less than ten parts per million. This is about the purity of the best spectrographic grade of solid graphite. Graphite cloth is relatively inexpensive so that each piece used may be discarded after each crystal has been grown. It is also rather absorbent, and discarding it after a single use is desirable so that the purity of successively grown germanium crystals is further assured.

The use of the graphite cloth results in a reduction in the dislocation density of the germanium crystal and an attendant improvement in lifetime. Germanium, like silicon, bismuth, and similar materials, expands when it solidifies and if the germanium crystal is confined, the expansion will set up considerable strain in it, resulting in a high dislocation density and low lifetime. The graphite cloth boat liner **42**, being resilient, gives during the expansion of the freezing germanium so that there is much less strain in the germanium, and the final grown crystal is thereby improved.

The use of the graphite cloth as a liner also has some thermal advantage during the crystal growing process. Being of a somewhat open texture as has any cloth, the liner has a moderate insulating quality and so it impedes the heat flow into the quartz boat and to some extent reduces the amount of heat conducted away from the crystal by the quartz. This causes the liquid crystal interface to be more nearly vertical during recrystallization which results in a crystal lattice which has fewer imperfections.

The graphite cloth which is used in the commercial embodiment has a weave of the type that the textile industry refers to as a "plain" weave. This is a weave such as would be found in an ordinary piece of cotton cloth. The graphite cloth contains no binder and has the following specifications:

Impurity content total weight	parts/million or less	10
Weight	oz./sq. yd	7.3
Guage	in	0.023
Tensile strength of warp	lbs./in	25
Tensile strength of fill	lbs./in	23
Electrical resistance @ 70° F.	ohms/sq	0.5
Strands per thread (braided together to form thread)		3
Filaments per strand		500
Filaments diameter	inches	0.0005

It has been found that carbon felt, and graphite felt may also be employed in the same manner as has the graphite cloth. These materials are not as yet available in quite as pure a form as the graphite cloth, however, and therefore, are not as desirable for use as boat lining for growing germanium crystals.

The melting and heating of the germanium material is accomplished by the furnace **27** (FIG. 1) which consists of a heater and an afterheater within a cylindrical insulated jacket **53**. The heater is comprised of two half-cylindrical heating eleemnts **54** and **55** which are brought together to form the cylindrical section shown in FIG. 6 surrounding the chamber **22**. The afterheater consists of a single half-cylindrical heating element **57**, and as shown in FIG. 7 is located in the furnace jacket **53** beneath the chamber **22** so that heat is directed upward toward the lower portion of the trough **38**. This is necessary so that as the crystal forms, the fall in temperature due to loss of heat from the germanium at the sides near the bottom will be retarded. If heat is not directed upward toward the lower sides of the trough, the liquid zone present during the crystal formation tends to be wider at the top than at the bottom giving rise to a crystal-liquid interface which may angle considerably with respect to the orientation of the desired crystallographic plane. This is undesirable since it results in a resistivity which is typically very much lower at the bottom of the crystal than elsewhere. However, with the afterheater heating element **57** properly adjusted, the liquid zone width is approximately the same at the top as at the bottom.

Returning again to the procedure: when the crystal growing boat **21** has been loaded, the apparatus **20** is charged by removing the end cap **28** from the chamber **22** and placing the loaded boat **21** in the chamber in the position shown in FIG. 1. In order that the finished crystal has an equilaterally triangular cross-section, it is necessary that the 60° included angle of the trough of the boat be so positioned that a vertical plane through the vertex of the trough will bisect that angle. The end cap **28** is then replaced and nitrogen is permitted to flow through the chamber **22** for a period of time sufficient to purge the chamber of any oxygen or water vapor which might react with the heated germanium during the crystal growing process. After sufficient purging of the chamber, the furnace **27** is moved to a particular location relative to the seed and ingot in the boat **21** by rotating the handwheel **25** of the lathe carriage **30**. In this position the hottest zone is approximately centered relative to the seed and ingot junction point, as shown in their original condition and position in FIG. 2. The furnace **27** is left in this position until some of the material on either side of this seed and ingot junction point and the germanium containing the dopant are melted together, and have reached equilibrium at which no further melting occurs. Then the mechanism which rotates the lead screw **29** is activated, and the half nut **26** on the lathe carriage **30** is engaged to feed the furnace very slowly down the length of the chamber **22**. As the furnace **27** travels along relative to the germanium charge in the boat **21**, the molten germanium cools slowly and monocrystalline germanium forms in the orientation dictated by the seed. The germanium is doped as required by the impurity introduced in the loading procedure. Most of the impurity travels along in the molten region, and the amount which remains behind in the crystal is determined primarily by the distribution coefficiency of the impurity.

After the furnace **27** has passed over the germanium and the germanium has cooled sufficiently, the boat **21**, plug **35**, and the germanium crystal are removed from the chamber **22** and the boat **21** is unloaded and the seed cut from the crystal. The completed single crystal of germanium **45** is shown in FIG. 3. It has substantially the same equilaterally triangular cross-sectional size and shape that the ingot had initially. A cut across this triangular bar of single crystal germanium perpendicular to the three sides will produce a wafer as **60** (FIG. 8), with major faces parallel to one of the {111} group of crystallographic planes. As previously mentioned, substantial improvement is found in the quality of germanium crystal so grown when the seed crystal **31** is oriented so that crystal growth commences in a manner so that faceting occurs at the corners of the triangular crystal rather than on the sides. The occurrence of twin crystals is substantially less, and so is the dislocation count in the crystal.

The crystal of equilaterally triangular section as thus grown is particularly desirable when cut into wafers **60**, and each wafer is substantially cut into round semiconductor dice **61**. The number of the circular die **61**, per unit area, cut from a wafer **60** is at a maximum with the lateral triangle shape for the cross-section, and hence the waste from a complete grown crystal of the present configuration is at a minimum. It is a simple thing to adjust the size of the triangular section in the present invention to give the maximum utilization of semiconductor material for a given dice size, since all that needs to be done is to increase or decrease the size of the cross-section of the triangular ingot **32** used in growing the crystal **45**. This may be done by placing more or less raw germanium material into the zone refining mold in which the polycrystalline ingot **32** will be cast during the zone refining process to prepare the germanium for subsequent crystal growing.

The two more commonly used crystal growing boats used in prior zone leveling apparatus have structures which are trapezoidal and semicircular in form, and when these crystals are cut or sliced into wafers, they provide respectively, germanium wafers **63** and **65** of the shapes shown in FIG. 9 and FIG. 10. Comparing the three wafer shapes **60**, **63** and **65** which are equal in area, FIG. 9 shows that the dice **61** in that cross-section are packed in the densest way possible, but there is still considerably more waste in the interstitial regions than there is in the interstitial regions of FIG. 8, or in the semicircular section of FIG. 10. The packing density of dice is fairly good in FIG. 10, but there is considerable waste along the edges of the wafer **65**, and in large production of semiconductor devices, and correspondingly large requirements for dice, this saving in waste is important. While fifteen dice of the size shown may be cut from the triangular wafer of a predetermined area, only twelve dice may be cut from either of the other two wafers of the same total area. A circular wafer (not shown), as cut from a grown germanium crystal of such cross-section must have an area slightly larger than the area of the triangle in order to provide the same number of dice of the size illustrated in FIGS. 8 to 10.

It is well-known that when semiconductor crystals are grown by the zone leveling process which is the type of process described here, the resistivity of the region very near the bottom of the crystal will usually be found to be much lower than elsewhere. Customarily this portion of the material is scrapped as it is usually too far out of manufacturing specification to be useable in the ultimate semiconductor device for which it had been intended. In FIGS. 9 and 10, note that this scrap region "*d*" represents a large percentage of the total crystal. In FIG. 9 four dice, or 33.3%, fall in the low resistivity region and cannot be used, and in FIG. 10 approximately 25% of the die cannot be used for the same reason. However, in FIG. 7, only one, or 6.6% of the whole, is wasted.

Comparing the total utilization of material for the triangular shape versus the other three shapes (trapezoidal, semicircular and circular), the triangular wafer will provide 75% more dice than the trapezoidal wafer, 55% more dice than the semicircular wafer, and 17% more dice than the circular wafer.

In one embodiment of this invention, the circular germanium die **61** as produced is used in the fabrication of power transistors presently being manufactured at the rate of more than a million per year. The dice used in their preparation are 260 mils in diameter, are of N type germanium having a lifetime of 50 microseconds, a dislocation density less than 8000 per square centimeter and a resistivity in the range of 9 to 14 ohm-centimeter. This germanium material is grown in a quartz boat **21** having a length of approximately 18 inches and a depth of about 1½ inches from a seed crystal **31** which is free of lineage and has a dislocation density less than 2000 per square centimeter. A triangular 40 ohm-centimeter N type ingot **32** of germanium is placed in the quartz boat **21** on the graphite cloth **42** so that it butts against the seed crystal **31**. The ingot **32** has substantially the same size cross-section as the seed. The small portion of germanium material **34** containing the N type doping agent antimony, which is placed at the seed-ingot junction point on top of the seed and the ingot, is about 12 grams in weight and has an antimony impurity concentration such that the resistivity is .005 ohm-centimeter. The graphite plug **35** which closes the end of the boat at the cylindrical portion has a diameter of about 2 inches and the triangular section **36** which fits in the boat is approximately the same size in cross-section as the ingot. In the particular apparatus used in preparing germanium for these transistors the chamber is of clear quartz about 75 millimeters inside diameter and is about 58 inches long.

After the chamber **22** of the apparatus **20** has been charged and the end cap **28** replaced, the chamber is purged of air by flowing nitrogen through it. After purging, nitrogen plus 5% hydrogen gas is passed through the chamber at a flow rate of about 4.5 liters per minute. Initial heating of the seed-ingot junction region is for 2 hours at 980° C. The hot zone is adjusted so that melting occurs for about 1 inch on either side of this region. After equilibrium has been reached, the crystal growing is completed by allowing the furnace to travel over the germanium at a rate of about 1 inch per hour.

During the period of time that the furnace **27** travels over the germanium and the crystal is growing, that part of the germanium which lies beneath the hottest part of the furnace will be molten for a region about 2½ inches in length except, of course, when the furnace is over the end of the ingot.

After the crystal **45** was formed and the furnace **27** has passed completely over the germanium, the motion of the furnace is stopped and the crystal is cooled in the hydrogen atmosphere of the chamber. After the crystal **45** is cool, the boat **21** is removed from the furnace and the crystal removed from it. The old seed crystal **31** is then cut from the new crystal **45** and the new crystal is classified according to resistivity, lifetime and dislocation density using well-known testing procedures.

A conservative example of the characteristics for germanium crystals made in accordance with this invention is shown below for triangular 20 ohm-centimeter resistivity crystals having a cross-sectional area of 1.25 square inches, and these characteristics exist over 75% of the length of each crystal:

Typical resistivity range cross-section (neglecting bottom-inch of crystal) ---percent--	±5
Lifetime (microseconds) ---	1500
Dislocation density, (number/square centimeter) --	500

What is claimed is:

1. Apparatus in which to grow a semiconductor crystal of triangular cross-section in a heating operation and while the apparatus is in a horizontal position, comprising in combination, a V-shaped trough to contain the crystal, said trough having straight sides which meet at an angle to form the bottom of the trough, means for closing the ends of said trough, and a removable carbon cloth lining in the trough to receive and contain crystal material in both hardened and in melted condition, and laying in said trough in a manner to physically separate said crystal material from the inside wall of said trough.

2. The structure for use in growing germanium single crystals by a zone leveling operation in a quartz boat so as to minimize the formation of twin and polycrystalline germanium crystals which would result from contact between molten germanium and the inside walls of a quartz boat used to contain the germanium, such structure comprising yieldable graphite cloth of a size to line the inside walls of a quartz boat having two sidewalls and being open at the top, and adapted to conform to the inside shape of the quartz boat when laid therein.

3. Apparatus in which to grow a monocrystalline semiconductor crystal by a zone-leveling type of growing operation comprising a receptacle with two side walls joined together at the bottom as a vertex of a triangle, and extending upwardly and outwardly therefrom in a V-shape

from said vertex to provide an open member to receive semiconductor crystal material therein to be heated for melting and then cooled for hardening, with said side walls being of heat resistant material,

means for selectively applying heat to portions of said receptacle intermediate said ends and proceeding from one end toward another one of said ends,

carbon cloth disposed everywhere over said side walls inside said receptacle wherein the semiconductor material is to be placed,

means closing said receptacle at each end to contain crystals from material therein when it is in a melted condition,

and one of said closing means at said one end including heat conductive material extending away from and engaging the crystal material to receive heat therefrom to form a thermal continuation of said crystal material.

4. A heat resistant boat in which is grown a crystal of substantially equilateral triangular cross section during the heating and cooling operation comprising a V-shaped quartz trough to contain and shape the crystal,

said trough having straight sides which are several times longer than they are wide which meet at an included angle of 60° to form a vertex at the bottom of the trough and having a liner of cloth-like material formed of carbon fibers,

means closing the ends of said trough so as to contain melted crystal material therein and means for supporting said trough during heating and cooling so that said included angle of 60° would be bisected by a vertical plane to the vertex of the trough.

5. In apparatus and material for the growing of monocrystalline germanium bar having a substantially equilateral triangular cross section and utilizing a germanium crystal growing charge for such growing,

a quartz boat having a V-shaped trough-like portion with an angle of 60° forming its V-shape with first closing means at one end thereof and a thermal conductive radiating closing means at the other end,

said thermal closing means comprising a block of graphite which fits into said trough but is free to move therealong during crystal growing operation,

and a removable graphite woven cloth-like liner on the inside of said trough and laying against the inside wall thereof to prevent germanium crystal material from touching the quartz of said boat.

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