

Dec. 10, 1957

L. P. HUNTER

2,816,050

METHOD OF FORMING MONOCRYSTALS

Filed Dec. 18, 1953

FIG. 1

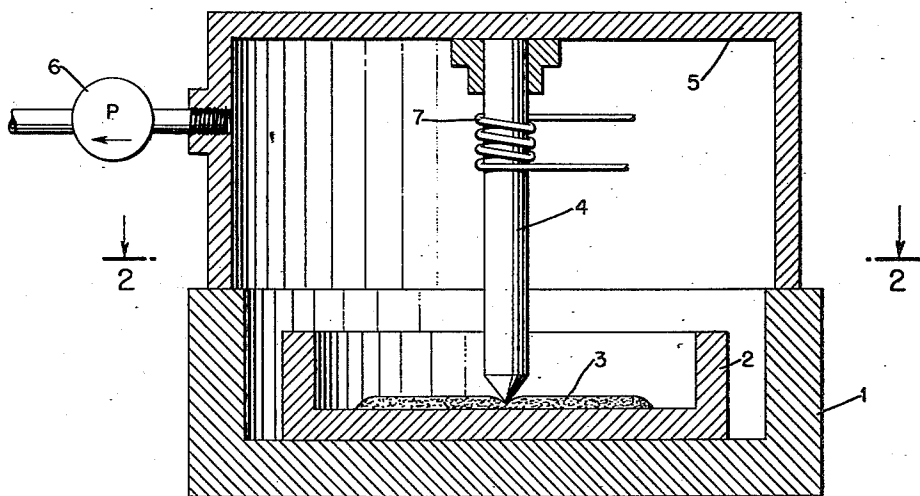
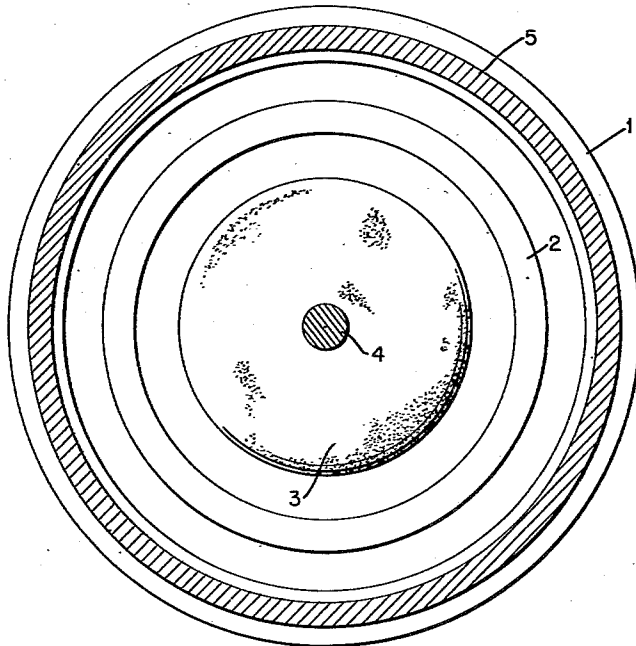


FIG. 2



INVENTOR.

LLOYD P. HUNTER

BY
P. E. Henniger
ATTORNEY

1

2,816,050

METHOD OF FORMING MONOCRYSTALS

Lloyd P. Hunter, Poughkeepsie, N. Y., assignor to International Business Machines Corporation, New York, N. Y., a corporation of New York

Application December 18, 1953, Serial No. 399,092

5 Claims. (Cl. 148—1.6)

This invention relates to forming of monocrystals, and especially to monocrystals of germanium and other semiconductive materials which are suitable for use in transistors and similar devices.

The peculiar electrical characteristics of transistors, which makes them suitable for use as amplifiers, oscillators, detectors and as non-linear electrical devices generally, occur with reliable uniformity only when the semiconductive body of the transistor is formed from a single crystal.

The common method for growing single crystals has been the Bridgeman method, which involves lowering a cone-shaped crucible containing molten material to be crystallized through a region in which a temperature gradient is maintained such that the upper portion of the region is above the melting point of the material, while the lower portion of the region is below that melting point. The Bridgeman method is not suitable for materials which expand on freezing, since the stresses developed in the material cause polycrystalline effects. For such materials, the common method of growing a single crystal, up to the present, has been the method discovered and described by Czochralski early in this century. Briefly, it consists of lowering a rod of pure germanium (or other material of which the crystal is being formed) into a crucible containing molten germanium. The crucible must be in a furnace having a controlled vertical temperature gradient such that the surface of the molten material in the crucible is at the melting point of germanium. The molten material below the surface is of course hotter than this melting point and the space above the surface is cooler. The rod of germanium is then very slowly retracted upward at a carefully controlled rate of speed, with the result that a single crystal of germanium is grown on the end of the rod. Great care must be exercised with that process, both with respect to temperature control and with respect to the motion of the rod, in order to prevent the development of a polycrystalline structure. The furnace temperature gradient must be continuously adjusted to compensate for the change in location of the surface of the molten material as the crystal is withdrawn from it.

It is an object of the present invention to provide an improved and simplified method of growing monocrystals.

Another object is to provide a method which will permit the use of simpler apparatus.

Another object is to provide improved and simplified apparatus for growing monocrystals.

The foregoing and other objects of the invention are attained by supporting a molten mass of the material to be crystallized so that it is laterally unconfined, and cooling the molten mass by extracting heat from a limited locality of the mass so that the solidification of the mass proceeds from that locality. More specifically, a mass of germanium, for example, is placed in the bottom of a crucible, the mass being small enough so that when melted it does not touch any of the lateral walls of the crucible. A rod of suitable heat conductive material,

2

preferably having a pointed tip, is brought into contact with a portion of the molten pool, and then heat is slowly extracted from a point on the rod remote from the pool. The pool gradually freezes to form a single crystal, the freezing action proceeding radially from the point of contact of the rod as a center. The crucible and the rod should be of a material which will not wet the material from which the crystal is being formed.

Other objects and advantages of the invention will become apparent from a consideration of the following specification and claims, taken together with the accompanying drawing.

In the drawing:

Fig. 1 is a somewhat diagrammatic vertical sectional view, through a furnace adapted to carry out the method of the present invention; and

Fig. 2 is a horizontal sectional view taken on the line II—II of Fig. 1.

Referring to the drawing, there is shown a heater or furnace 1 of generally cylindrical form in which is located a cylindrical crucible 2. On the bottom of the crucible 2 and spaced from the lateral walls thereof is a molten pool 3 of germanium or other material to be crystallized. Projecting downward into contact with the pool 3 is a rod 4 having its lower end pointed, and attached at its upper end by suitable means to a cover 5 for the furnace 1. Means is provided for evacuating this space within the cover 5 of the furnace 1. The evacuating means may be of any suitable construction and is illustrated diagrammatically as including a vacuum pump 6. The upper end of the rod 4 is provided with a cooling coil 7 of suitable construction. Although shown as an external coil, the cooling mechanism may take other forms, and may, for example, be within the rod 4.

In carrying out the method of forming a monocrystal according to the invention, a quantity of germanium is placed in the bottom of the crucible 2 and the crucible is then placed in the furnace 1. The cover 5 with the attached rod 4 and evacuating pump connections is then placed on the heater 1. The space within the heater 1 and the cover 5 is then evacuated to a suitable degree and the heater is then started to bring the germanium 3 to its melting point. Any suitable heating means and temperature control means may be used, since such means forms no part of the present invention. The entire interior of the furnace should be maintained substantially at the melting point of germanium.

The quantity of germanium placed in the crucible 2 should be such that when melted it will form a pool 3 which does not touch any of the lateral walls of the crucible. Heat is extracted from the pool through the rod 4 by cooling its upper end, as for example by means of the cooling coil 7. It is desirable to extract heat slowly, without any sudden drop in temperature at any locality within the furnace. As the heat is extracted, the germanium in the pool freezes. It freezes first adjacent the tip of the rod 4, and the freezing progresses outwardly.

Germanium expands on freezing by approximately 10% of its volume. In order that the crystal formed from the pool 3 may be a complete monocrystal, it is necessary that the edges of the pool never touch the walls of the crucible at any time during the cooling process. Consequently, the mass of material in the pool must be smaller than the mass required to cover the bottom of the crucible. The mass of germanium employed should be smaller than the bottom of the crucible not by the exact amount of space required for expansion of the germanium on cooling, but an additional four or five percent of the area of the crucible should be allowed for error.

If one edge of the pool touches one wall of the crucible during the cooling process, a polycrystalline formation will develop at that edge. The pool may form

a usable monocrystal throughout most of its structure, but it will be polycrystalline wherever it is laterally confined.

In order that the liquid pool will not spread out and touch the walls of the crucible, the crucible must be of a material which does not wet the material of which the crystal is being formed. The rod also should not be wet by the germanium. It is also desirable that the crucible and the rod be of material which will not contaminate the crystal. In the case of germanium, graphite or carbon is preferred for both the crucible and the rod from both these standpoints.

While the present method is not necessarily limited to use with materials which expand on freezing, it finds its greatest advantage with such materials.

The evacuation of the furnace during the melting process is used only to prevent contamination of the germanium by the air or other gas in the furnace. Where contamination of the material by the gases in the furnace is not a problem, evacuation may be omitted.

The bottom of the crucible 2 on which the pool rests may be either flat or slightly concave. If the concavity is sufficient to partially confine the melt, polycrystalline effects are likely to develop.

The general temperature within the furnace should be maintained at the melting point of the material during the freezing process. The slow extraction of heat from one point in the germanium pool can then be readily effective to freeze the entire pool.

While I have shown and described a preferred embodiment of my invention, other modifications thereof will readily occur to those skilled in the art and I therefore intend my invention to be limited only by the appended claims.

I claim:

1. The method of forming a monocrystal comprising the steps of forming in a furnace a laterally unconfined pool of molten crystallizable material, maintaining the atmosphere in said furnace substantially at the melting point of said material, bringing a pointed member of heat conducting material into contact with the pool, and thereafter solidifying said pool by slowly extracting heat from a limited locality of said pool by cooling a portion of said member spaced from said pool.

2. The method of forming a monocrystal as defined in claim 1, in which said member is formed of a material which does not contaminate the crystallizable material.

3. The method of forming a monocrystal as defined in claim 1, in which the material is germanium.

4. The method of forming a monocrystal as defined in claim 1, in which said furnace and said member are of material which does not wet the material of which the crystal is being formed.

5. The method of forming a monocrystal as defined in claim 1, in which said member is formed of graphite.

References Cited in the file of this patent

UNITED STATES PATENTS

303,607 Arencibia ----- Aug. 19, 1884

OTHER REFERENCES

Proceedings of the Royal Society of London, article by Kapitza, Series A, vol. CXIX, pages 362, 363.

Buckley: Crystal Growth, pub. 1941, pages 86-89.