

May 25, 1954

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2,679,080

PRODUCTION OF SINGLE CRYSTALS OF GERMANIUM

Filed Dec. 30, 1949

FIG. 1

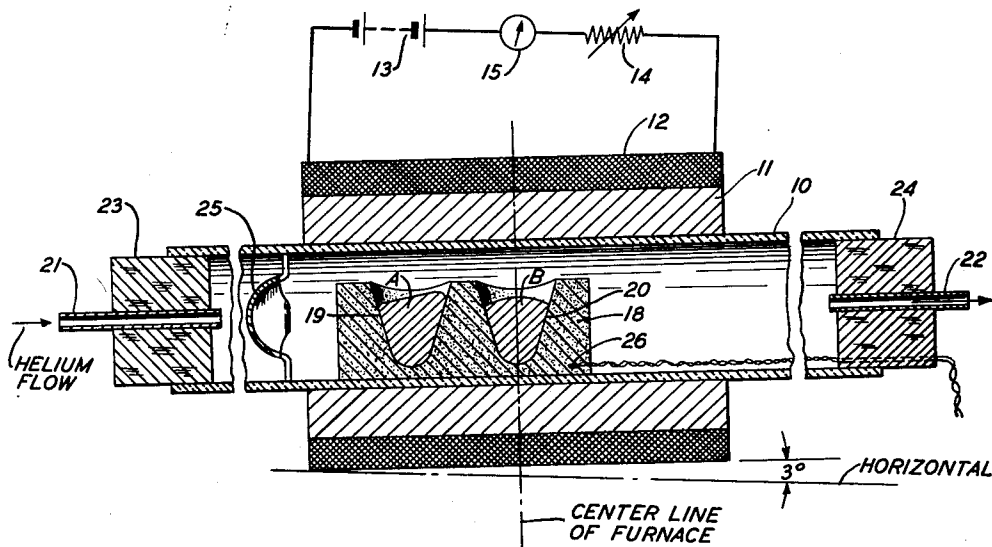


FIG. 2

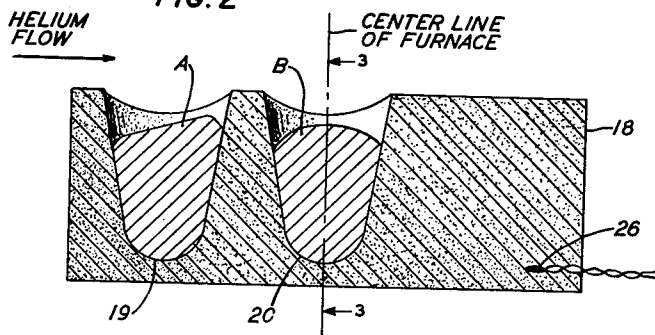


FIG. 3

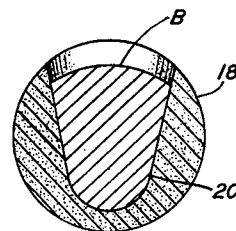
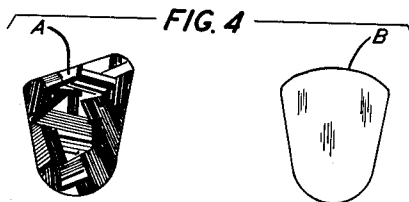


FIG. 4



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2,679,080

PRODUCTION OF SINGLE CRYSTALS OF
GERMANIUM

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Application December 30, 1949, Serial No. 136,127

5 Claims. (Cl. 22-212)

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This invention relates to an improved method and apparatus for the production of large single crystals of fusible materials, particularly of germanium, which is an element important in the manufacture of electrical translating devices such as rectifiers, transistors and the like.

While the method is applicable to the production of large single crystals of other elements and of compounds, with appropriate choice of temperature, of atmosphere about the crystallizing substance, etc., it will be described in the specific application to crystals of germanium, because that element is especially prone to twinning when allowed to solidify from the molten condition.

A general object of the invention is to provide a method and apparatus for the production of large single crystals of a metal or of a salt.

A feature of the invention is the provision of a "dummy load" of the same material as that of which a single crystal is desired and of substantially the same mass. The dummy load is melted under the same conditions as is the mass, conveniently termed the "active load," which is to become the desired crystal. The arrangement is such that the freezing of the dummy load begins and progresses slightly in advance of the freezing of the active load, giving up its latent heat of fusion continuously to stabilize the thermal conditions under which the active load solidifies, at a temperature closely corresponding to the melting point of the material. It is obvious that the thermal conditions can be varied as desired by altering the mass of the dummy load and by changing its location.

Another feature of the invention is that the masses of material are mechanically undisturbed during solidification, and are therefore not subject to the external mechanical forces which are known to be detrimental to single crystal formation.

It has long been known that large crystals can be produced by slowly withdrawing molten material from the high temperature environment in which it was melted; this method is described by Bridgman in the Proceedings of the American Academy of Arts and Sciences, volume 60, page 305, 1925. This method is unsuited for use with germanium because too large a temperature gradient is produced and because of the danger that mechanical vibrations may upset the crystal growth.

A particular object of this invention is therefore to make possible the formation of massive single crystals of germanium with substantially ideal freedom from mechanical and thermal disturbances.

The invention will be understood from the

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following description of a preferred embodiment, with reference to the accompanying drawing in which:

Fig. 1 is a schematic diagram of apparatus illustrative of the invention, as arranged in an actual case;

Fig. 2 is an enlarged partial view in longitudinal section of the graphite crucible shown in Fig. 1, showing the form assumed by the loads on solidifying;

Fig. 3 is a view, to the same scale as Fig. 2, of a transverse section of the crucible; and

Fig. 4 is a pictorial view, in section paralleling that of Fig. 2 and to the same scale, of the crystal bodies obtained.

Referring to Fig. 1, 10 designates a quartz tube 72 inches long and of 1.75 inch internal diameter installed in a conventional electric furnace 11, the controllable heating facilities for which are symbolically represented by coil 12 supplied with heating current by source 13 through variable resistance 14 and ammeter 15. Furnace 11 is suitably 22 inches x 10.5 inches pierced centrally by a 2.125-inch diameter hole through which tube 10 is inserted.

A graphite crucible cylinder 18, of length about 4 inches and diameter (about 1 inch) conveniently less than that of tube 10, is excavated to have two substantially similar thimble-shaped cavities 19 and 20, filled respectively with germanium ingots A and B. Ingots A and B may be buttons or polycrystalline masses of germanium of the highest attainable purity. Ingot B, which will result in the desired crystal, is centered on the furnace transverse center line.

Helium, from a source not shown, is admitted through a small diameter tube 21, flows over the crucible and its loads and escapes through a like tube 22, both tubes 21 and 22 entering tube 10 through ports 23 and 24, respectively. The helium stream, distributed by quartz baffle 25, washes air from tube 10 and provides an inert atmosphere for the melting and subsequent freezing of A and B. Thermocouple 26, embedded in cylinder 18, measures the temperature of the crucible; its terminals lead to a meter not shown. The whole apparatus of Fig. 1 is inclined three degrees to the horizontal, so the helium flows upward.

The germanium specimens to be melted are first etched in a standard hydrofluoric-nitric acid bath to remove foreign surface materials, then placed in their respective cavities in crucible 18 and inserted into tube 10 far enough for cavity 20 to be centered on the furnace center line. The flow of helium, about one-half liter per minute, is as shown in Fig. 1 from left to right; the helium wind thus blows from ingot A to ingot B.

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The temperature of the crucible is now raised to 980° C., which is about 30° C. above the melting point of germanium, and kept there for five hours to insure the establishment of thermal equilibrium. The masses filling cavities 19 and 20, now molten and at a steady temperature, are then allowed to cool at the rate of 5 to 10° C. per hour; this is effected by gradually decreasing the power supplied to coil 12. When the temperature has fallen to 900° C., the graphite crucible is allowed to cool more rapidly to room temperature. Then the crystal bodies are removed and their respective characters are determined.

Fig. 2, to a larger scale than Fig. 1, shows the cavities 19 and 20 with the solidified masses A and B. Fig. 3 is a transverse section of crucible 18 taken at the center line in the direction of the arrows. Mass A is the first to cool because the temperature within the furnace is highest at the center line and falls slightly toward each end of tube 10, and in part also because the flow of helium is from left to right and reaches first cavity 19. Mass A, in cooling through the melting point, gives up its latent heat of fusion exactly at the melting point to the helium and to crucible 18. The later freezing mass B is thus enabled to solidify under perfectly stable thermal conditions, while Mass A is exposed to possible thermal disturbances. That this is true is clearly shown by the sections of A and B in Fig. 2 where the masses, having horizontal surfaces when molten, have solidified differently: mass A unsymmetrically and peaked at the surface portion last reached by the helium, mass B symmetrically with a surface convex upward. The convexity is due to the fact that germanium expands on freezing and the depth of the melt is greatest at the center of cavity 20.

The configurations shown in Figs. 2 to 4 for the masses A and B are those found at the end of an actual melt. It is to be expected that masses A and B will differ in crystalline structure because B is protected by A which is not protected at all. This is actually the result, as shown in Fig. 4 in which are depicted with approximate fidelity the etched appearances of the crystal masses in sections made by a diamond saw cutting each mass in a central vertical plane. Mass A is polycrystalline, mass B is a single crystal.

It is to be understood that other gases than helium, or vacuum, and other than graphite crucibles, may be used. What is required is a gas (when one is used) providing an inert or a reducing atmosphere, and preferably of low specific heat. The crucible should have high heat conductivity and be of material which does not shed impurities into the germanium. While a quartz tube is preferred, this is used for the sake of avoiding contamination of the germanium. An induction furnace may be used for heating the crucible and loads, provided the frequency of the heating power is chosen high enough to avoid producing agitation of the molten germanium.

Single germanium crystals prepared as above described, when tested as rectifiers, are found to have high peak back voltages above 100 volts and in some cases as high as 300 volts. The material of the ingots was, in the tests made, found to have predominantly P-type rectification; N-type ingots could be made by slow cooling of the germanium to room temperature. Polycrystalline ingots invariably are formed when substantial temperature gradients are intentionally created.

It is obvious that a reducing atmosphere, such

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as hydrogen, may be employed if it is desired to make certain that no germanium oxide shall exist in the melt after temperature equilibrium has been established. The atmosphere should not react chemically with the germanium.

What is claimed is:

1. The method of preparing a single crystal of germanium which comprises placing a first and second substantially equal but distinct mass of germanium in a chamber, positioning said masses in said chamber so that the first mass is in a portion of said chamber which cools at a faster rate than that portion containing said second mass, said first and second masses being contained in crucibles which are inert to germanium and are in contact with each other and being separated by a distance of the order of their individual widths thereby to establish an effective heat transfer relationship between the masses, melting the masses in the chamber while continuously passing helium over them at a rate of about one-half liter per minute, directing the flow of helium successively over the first and second masses, maintaining the molten masses at a temperature of about 980° C. for a period of about five hours to establish thermal equilibrium, maintaining the melted second mass in a substantially quiescent state immediately preceding and during its freezing, cooling the chamber in the vicinity of the first mass at a rate of the order of 5° C. per hour from a temperature of about 980° C. to about 900° C. to initiate freezing in said first mass prior to the initiation of freezing in said second mass, cooling said second mass to its freezing temperature while said first mass is freezing, maintaining the temperature of the second mass substantially at the freezing temperature of germanium over a substantial interval by transmitting a portion of the latent heat of fusion evolved in the freezing of the first mass to the vicinity of the second mass.

2. In the method of preparing single crystals of fusible crystallizable material by freezing a melt of said material at a slow and uniform rate, the steps which comprise positioning a melt of said material in a chamber containing an atmosphere consisting of a gas which does not react chemically with said material, positioning a second melt of like material and of a size substantially equal to said first melt in the chamber adjacent said first melt and in a portion of said chamber having a higher cooling rate than that portion containing said first melt, containing both of said melts in contracting crucibles which are inert to said material to establish an effective heat transfer relationship between said melts, passing said atmosphere successively over said second and first melts, maintaining said first melt in a substantially quiescent state immediately preceding and during its freezing, and reducing the temperature of the chamber in the region of said second melt at a rate of the order of 5° C. per hour to initiate freezing in said second melt prior to the initiation of freezing in said first melt, cooling said first melt to the freezing temperature of the material to initiate freezing in said first melt while said second melt is freezing, and stabilizing the temperature of the environment of said first melt substantially at the freezing temperature of the material by transmitting a portion of the latent heat of fusion evolved in the freezing of the second melt to the vicinity of the first melt.

3. The method of preparing single crystals of germanium which comprises preparing two similar and substantially equal but distinct masses of

germanium, melting the masses in containers of material inert to germanium in a flow of helium and in alignment with the direction of flow, maintaining the containers in contact and the masses at a separation substantially equal to their dimensions in the direction of helium flow to establish an effective heat transfer relationship between said masses, maintaining the molten masses at a temperature above the melting point of germanium for a period of about five hours to establish thermal equilibrium, slowly cooling the mass first reached by the helium to the freezing temperature of germanium to initiate freezing therein prior to the initiation of freezing in the mass last reached by the helium, maintaining the mass last reached by the helium in a substantially quiescent state immediately preceding and during its freezing, initiating freezing in the mass last reached by the helium during the freezing of the mass first reached by the helium, and stabilizing the temperature of the environment of said mass last reached by the helium substantially at the freezing temperature of germanium by transmitting to said mass a portion of the latent heat of fusion evolved in the freezing of the mass first reached by the helium, thereby obtaining as a single crystal of germanium the mass last reached by the helium.

4. The method of preparing single crystals of germanium which comprises preparing two similar and substantially equal but distinct masses of germanium in crucibles which are inert to germanium, melting the masses in a flow of gas incapable of combining chemically with germanium, maintaining the crucibles in alignment with the direction of gas flow and in contact to establish an effective heat transfer relationship between the masses, maintaining the molten masses at a temperature above the melting point for a period of about five hours, reducing the temperature in the vicinity of the mass first reached by the gas at a rate of about 5° C. per hour to initiate freezing therein prior to the initiation of freezing in the mass last reached by the gas, maintaining the mass last reached by the gas in a substantially quiescent state immediately preceding and during its freezing, initiating freezing in the mass last reached by the gas during the freezing of the mass first reached by the gas, and stabilizing the temperature of the mass last reached by the gas substantially at the freezing temperature of germanium by transmitting to said mass a portion of the latent heat of fusion evolved in the freezing of the mass first reached

by the gas, thereby obtaining as a single crystal of germanium the mass last reached by the gas.

5. The method of preparing single crystals of fusible crystallizable material which comprises melting a plurality of similar and substantially equal and distinct masses of said material in containers of material inert to said fusible material while in a flowing atmosphere incapable of combining chemically with the fusible material, maintaining said containers aligned in the direction of atmospheric flow and in contact to establish an effective heat transfer relationship between said masses, maintaining all of the molten masses at approximately the same temperature above the melting point for a period of about five hours to establish thermal equilibrium, maintaining the melted masses in a substantially quiescent state until they are frozen, slowly cooling a first of said masses to the freezing temperature of said material to initiate freezing therein while maintaining the remaining masses above the freezing temperature of the material, cooling the next succeeding mass to the freezing temperature of the material while the respective next preceding mass is freezing, and stabilizing the temperature in the vicinity of said next succeeding mass at the melting temperature of the material by transmitting the latent heat of fusion evolved from the freezing of the next preceding mass to the vicinity of the mass.

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