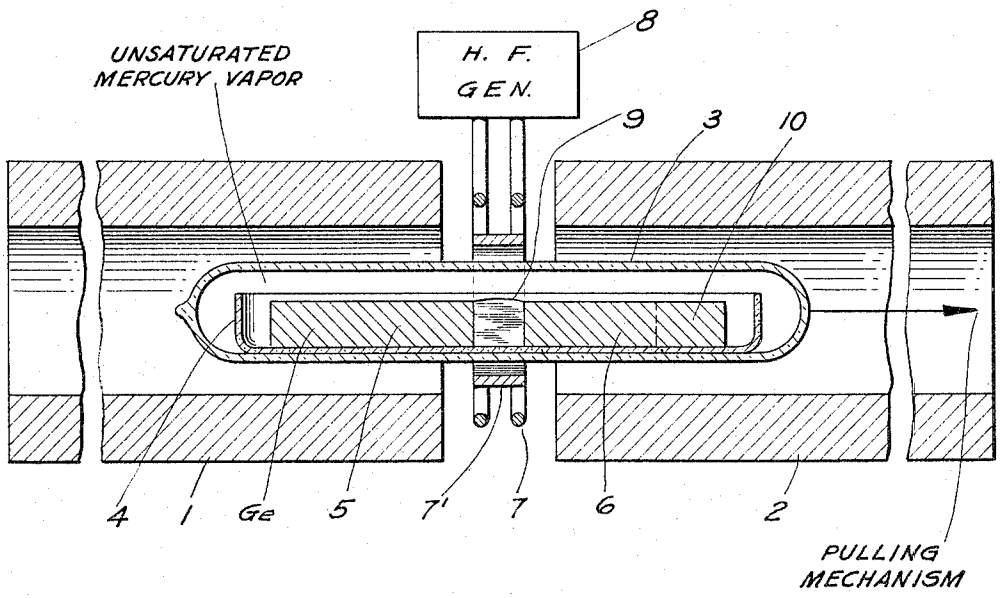
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METHOD OF MAKING MERCURY-DOPED GERMANIUM SEMICONDUCTOR CRYSTALS

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# METHOD OF MAKING MERCURY-DOPED GERMANIUM SEMICONDUCTOR CRYSTALS

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This invention relates to mercury-doped germanium semiconductor crystals for use as photoconductive infrared detectors, and in particular to a novel method of making the crystals.

Mercury-doped germanium semiconductor crystals exhibit excellent properties for the detection of infrared in the range of 8.5 to 13.5 microns, which corresponds to the self-emission of radiation of near ambient temperature sources. When the detector is maintained at 35° Kelvin or lower, its sensitivity is extremely high, while its time constant remains very small. The assembly comprises cooling apparatus capable of providing a cold finger at a temperature of 35° K. or less, such as the Norelco miniature Cryogenerator refrigeration unit, on which cold finger is mounted a single crystal of the mercury-doped germanium semiconductor with a pair of associated electrode contacts thereto. For best results, the mercury doping of the germanium should lie in the range of about $1\times10^{14}$ to $5\times10^{15}$ atoms of mercury/cubic centimeter of germanium.

Manufacturing single crystals of germanium doped with the foregoing concentration of mercury is a difficult task. Two techniques have been described in the prior art to accomplish this, both of which involve certain difficulties. In the first, a zone-leveling method with an open system is employed. The germanium is grown by zone-leveling in an open boat containing a source of mercury while an inert or reducing gas is flowed through the boat. The mercury source, located near the gas inlet, is heated, vaporizing mercury, and the flowing gas carries the mercury vapor over the growing crystal causing a certain quantity of the mercury to enter the crystal. This method suffers from the disadvantage of requiring large quantities of mercury to sustain one atmosphere pressure in the growth region, affording a serious problem of safe disposal of the mercury vapor and the other hazards that accompany working of large quantities of mercury, which is very toxic.

In the second technique, a sealed vessel or bomb method is employed. The germanium is again grown by zone-leveling in a sealed vessel containing a pair of mercury reservoirs. The vessel is heated at a temperature establishing the desired mercury vapor pressure in equilibrium with the mercury liquid reservoir. However, because the saturated vapor is involved, whose pressure varies exponentially with the absolute temperature of the coldest spot of the vessel, even small fluctuations in the vessel temperature cause very large variations in the mercury vapor pressure, which determines the mercury concentration in the grown crystal. For instance, as reported by one worker, at a temperature of 300° C. each degree change in temperature causes a change in vapor pressure of roughly 5 mm. mercury. Thus, extreme precautions have to be taken to ensure accurate control and stability of the vessel temperature.

I have invented a technique which tremendously reduces the temperature sensitivity of the mercury vapor pressure control while affording safe containment and disposal of the toxic mercury. In my invention, I provide a method in which the germanium crystal is grown in a hermetically-sealed vessel containing a weighed charge of mercury. The quantity of mercury provided is chosen so that, at the minimum temperature of any region of the vessel during the growth process, the mercury is fully evaporated to produce an unsaturated vapor in the vessel. No condensed or liquid phase of the mercury is present. As a consequence, the pressure of the mercury vapor varies only linearly with the coldest spot of the vessel, rather than exponentially in the case where a saturated vapor is present. Thus, the vapor pressure is made relatively insensitive to temperature, enabling with a relatively simple and inexpensive apparatus to control accurately the mercury pressure and thus the final mercury concentration in the growing crystal. Single crystals of germanium with more uniform mercury doping are thus obtained, making for a higher yield of suitable active elements for this detector application.



The invention will now be described in greater detail with reference to the accompanying drawing, which shows schematically, one form of apparatus for carrying out the method of the invention.

The sole figure of the drawing depicts a modified zone-leveling apparatus suitable for manufacturing the mercury-doped germanium crystals in accordance with the invention. It comprises a tubular furnace including aligned heater sections 1 and 2. Mounted for longitudinal horizontal movement within the furnace by means not shown is an elongated quartz vessel or capsule 3. The vessel or capsule 3 is sealed hermetically and contains within it a quartz boat 4 which contains a polycrystalline charge of zone-refined germanium 5 adjacent to a single crystal of germanium 6. Located between the heater sections 1 and 2 is a high-frequency induction coil 7 connected to a high-frequency generator 8. Within the coil 7 is mounted a graphite susceptor ring 7'. When the coil 7 is excited by the generator 8, the susceptor 7' is heated and in turn establishes a molten zone 9 in the germanium charge 5. Means are provided connected to the right-hand end of the vessel 3 for slowly pulling it through the center of the furnace and to the right of the figure, and thus the molten zone is advanced through the germanium charge in a conventional zone-leveling technique causing the conversion of the poly-crystalline germanium into a single germanium crystal.

A weighed charge of mercury is provided within the sealed vessel 3. The quantity of mercury provided is chosen so that at the temperature of the coldest spot of the vessel 3, the mercury remains fully vaporized producing an unsaturated vapor within the vessel 3. The molten zone 9 is thus subjected to the mercury vapor and absorbs a certain amount of the mercury, i.e., a certain amount of the mercury dissolves in the liquid zone 9. A portion of the mercury remains in solution when the liquid zone freezes and solidifies thus establishing a certain concentration of the mercury in the grown crystal 6.

Initially, the polycrystalline charge of germanium is refined to a degree that all known electrically active impurities are reduced to a concentration level of the order of a factor 10 below the desired mercury concentration. In the application intended for the mercury-doped germanium, it is important that the germanium be extremely pure lest the effects produced by other impurities mask those desired of the mercury levels. For instance, if the desired mercury concentration is $8\times10^{14}$ atoms/cc., then it would be preferable to reduce the concentration level of active impurities in the starting ingot to about $8\times10^{13}$ or below, the relative difference depending in general upon the nature of the impurity. If the undesired impurity has a low segregation coefficient, then the subsequent zone-leveling treatment during which the mercury is added will tend to sweep such impurity to one end of the ingot and thus effectively remove it. In the latter case, a higher concentration of the undesired impurity can be tolerated due to the refining action of the melting

treatment. Germanium with the required low concentration of impurities can be obtained if desired from present commercial suppliers of semiconductor materials. Such germanium generally exhibits a resistivity in excess of 40 ohm-cm. as measured at a temperature of 20° C.

A single oriented seed crystal, indicated by reference numeral 10, is disposed in the right-hand end of the boat 4 and adjacent and in contact with it is the polycrystalline charge. The quartz boat 4 may be carbonized on its interior to prevent sticking of the germanium. Next the weighed supply of the mercury is provided within the vessel 3. The interior of the vessel 3 is purged with dry hydrogen, and then evacuated or partially filled with an inert gas at a low pressure, after which it is permanently sealed off. Then the vessel 3 is disposed in the furnace such that the single seed crystal end 10 is underneath the susceptor 7'. The heater sections 1 and 2 are then energized to establish the minimum temperature prevailing at any point within the vessel during the growth process of the crystal from the melt, which controls the pressure of the mercury vapor inside the vessel. Thus, it is necessary that the furnace be of sufficient length so that the entire capsule remains within the heater sections while it is being pulled through the furnace to ensure that the coldest spot of the vessel is indeed controlled by the heater sections 1 and 2. The vessel temperature is chosen so that the entire supply of mercury is vaporized to establish an unsaturated vapor within the vessel. While the pressure of the unsaturated vapor is preferably chosen near the pressure of the saturated vapor, i.e., as high as is possible, sufficient separation should be maintained to prevent any condensation of the mercury and thus a liquid mercury phase within the vessel. The vapor pressure of tthe mercury can be controlled either by changing the quantity of mercury introduced, or by changing the temperature of the coldest spot of the vessel by the heater sections 1 and 2. Pressure variations between about 1 and 760 mm. mercury are readily obtained. As an unsaturated vapor is present, its pressure is only a linear function of the vessel temperature, in contrast to the exponential relationship between the vapor pressure and temperature that prevails when the saturated vapor is present, which makes control and stability of the mercury vapor pressure exceedingly difficult to obtain. In the inventive method, accurate control of the vapor pressure of the mercury over the germanium melt from which the crystal is grown is readily obtained. Since the solubility of the mercury in the germanium melt is proportional to its vapor pressure over the melt (Henry's law), and since the concentration of the mercury impurity entering the crystallized solid portions formed in equilibrium with the melt by freezing is related to the concentration of the mercury in the melt by the segregation coefficient (a constant), it is therefore seen that the mercury concentration in the germanium grown single crystal is directly related to and determined by the vapor pressure of the mercury over the melt at the time of solidification of the solid-crystal phase from the melt.

After the vessel 3 has been pulled completely through the furnace, and the molten zone 9 caused to traverse the entire length of the germanium charge starting from the seed crystal end 10, producing a complete grown single crystal 6, then the furnace may be deenergized and allowed to cool to room temperature. The germanium crystal is removed from the vessel 3, the beginning and end portions cropped off, and the remainder may be employed to produce the active detecting elements. To this end, the ingot is generally sliced to form thin wafers whose major surfaces coincide with crystal planes of the germanium crystals, such as the [111] plane. Then the thin wafers are generally diced to form tiny rectangles having the dimensions desired for the particular application. For instance, the elements might have dimensions of 10 mm. by 10 mm. by 5 mm. The surfaces of the elements are generally etched to remove any work damaged areas arising, and a pair of ohmic contacts made to opposite ends. A platinum wire soldered by means of indium is suitable for this purpose. After cleaning and drying, the assembly is encapsulated in the usual way to protect against contamination. Then it is ready for mounting in or on the cooling means. To ensure adequate transmission of the desired infrared to the active mercury-doped germanium element, suitable infrared transmissive windows, for instance of barium fluoride, should be employed in the envelope.

As indicated earlier, it is preferred that the mercury concentration lies generally in the range of $1\times10^{14}$ to $5\times10^{15}$ atoms of mercury per cc. of germanium. I have successfully manufactured samples of germanium with such a mercury-doped concentration with the apparatus disclosed in the drawing under the following conditions. The volume of the vessel 3 was 200 cc. The volume taken up within the vessel by the boat 4 and germanium charge was approximately 50 cc. The quantity of mercury introduced was 0.100 gram. The vessel 3 was maintained at a temperature of 370° C. The size of the molten zone 9 was approximately 20 mm., and the vessel was pulled at a rate of 2 cm. per hour. Sections cut from the resultant single crystal contained a concentration of $1\times10^{14}$ atoms of mercury per cc. and exhibited a resistivity of 28 ohm-cm. In other runs, the vessel temperature and all other things being maintained the same, a quantity of mercury of 0.300 gram was employed, producing a mercury concentration of $3\times10^{14}$ atoms per cc. of germanium. With the vessel again maintained at the latter temperature, and increasing the quantity of initially-provided mercury to 0.600 grm, a mercury concentration of $9\times10^{14}$ atoms per cc. of germanium was obtained. The mercury vapor pressures produced varied between about 0.2 and 1 atmosphere. In successive runs made under very similar conditions, excellent reproducibility of mercury-doping was obtainer.

It will thus be evident from the foregoing description that the method of the invention offers a number of important advantages over the prior art techniques for manufacturing controlled-mercury-doped single crystals of germanium. Further, only small amounts of mercury are required thus avoiding any harmful release of the toxic mercury in the event of an accident. No problems of safe disposal of the mercury vapor are encountered since it is always contained within the sealed vessel. Harmful contamination of the germanium is also reduced by the closed system employed. The apparatus employed is relatively simple and no special care is required to maintain the desired vessel temperature and thus the accurately-controlled vapor pressure of the mercury impurity.

While the growing of mercury-doped germanium crystals by zone-leveling is described, it will be understood that the principles enunciated herein are applicable to the growing of germanium crystals in an atmosphere of unsaturated mercury vapor by other well-known techniques, such as the vertical pulling or Czochralski technique, the floating-zone technique, and well-konwn modifications thereof. It will also be understood that, while I have described my invention in connection with specific embodiments and applications, other modifications thereof will be readily apparent to those skilled in this art without departing from the spirit and scope of the invention as defined in the appended claims.

What is claimed is:

1. A method of growing mercury-doped germanium semi-conductor crystals, comprising the step of crystallizing the germanium from a melt in a sealed system containing a weighed charge of mercury as the active dopant while maintaining the minimum temperature prevailing within any point of the system at a value at which the total mercury charge is fully vaporized establishing within the sealed system over the melt an unsaturated vapor of mercury whose pressure is determined by the said minimum temperature to dissolve in the melt an accurately controlled quantity of mercury.

2. A method as set forth in claim 1 wherein the pressure of the mercury vapor is such that the mercury concentration in the grown crystal is between $1\times10^{14}$ and $5\times10^{15}$ atoms/cc. of germanium.

3. A method as set forth in claim 2 wherein the pressure of the mercury vapor pressure lies between 1 and 760 mm.

4. A method of making mercury-doped germanium semi-conductor signle crystals with a mercury concentration between about $1\times10^{14}$ and $5\times10^{15}$ atoms of mercury per cc. of germanium for use as the active element of an infrared detecting system, comprising the steps of introducing into a vessel a refined polycrystalline charge of germanium, providing within the vessel in contact with the polycrystalline charge a single seed crystal of germanium, introducing into the vessel a weighed charge of mercury as the active dopant, sealing the vessel, heating the vessel such that the coldest spot within the vessel is maintained at a temperature at which the weighed charge of mersury is fully vaporized establishing over the germanium charge a pressure of unsaturated mercury vapor whose value is determined by the temperature of the coldest spot, and establishing a molten zone at the junction of the seed crystal and the germanium charge and advancing the molten zone through the polycrystalline charge from the seed crystal end to grow by zone-levelling an elongated single crystal of germanium containing mercury in the aforementioned concentration range.

5. A method as set forth in claim 4 wherein the pressure of the mercury vapor is between about 0.1 and 1 atmosphere.

6. A method of making mercury-doped germanium semi-conductor single crystals with a mercury concentration between about $1\times10^{14}$ and $5\times10^{15}$ atoms of mercury per cc. of germanium for use as the active element of an infrared detecting system, comprising the steps of introducing into a vessel a polycrystalline charge of germanium refined to the degree that all known electrically active



impurities are reduced to a concentration level below about $1\times10^{13}$ atoms per cc. of germanium, providing within the vessel in contact with the polycrystalline charge a single seed crystal of germanium, introducing into the vessel a weighed charge of mercury as the sole active dopant, sealing the vessel, heating the vessel such that the coldest spot within the vessel is maintained at a temperature at which the weighed charge of mercury is fully vaporized establishing over the germanium charge an unsaturated vapor of mercury whose pressure is close to that of a saturated vapor at the same temperature, establishing a molten zone at the junction of the seed crystal and the germanium charge and advancing the molten zone through the polycrystalline charge from the seed crystal end to grow by zone-leveling an elongated single crystal of germanium, the pressure of said unsaturated mercury vapor established over the melt during the growth of the crystal having a value at which the amount of mercury dissolved in the melt produces the desired mercury concentration in the thus-grown single crystal of germanium.


**References Cited by the Examiner**

UNITED STATES PATENTS

| | | | |
|---|---|---|---|
| 2,379,088 | 3/1956 | Pfann | 148—1.5 |
| 2,834,697 | 5/1958 | Smits | 148—189 |
| 2,844,737 | 7/1958 | Hahn et al. | 252—623 |
| 2,873,222 | 2/1959 | Derick et al. | 148—189 |
| 2,921,905 | 1/1960 | Chang | 252—62.3 |
| 2,954,308 | 9/1960 | Lyons | 148—189 |
| 3,108,073 | 10/1963 | Vanik et al. | 252—62.3 |
| 3,113,056 | 12/1963 | Van Doorn | 252—62.3 |
| 3,154,446 | 10/1964 | Jones | 148—189 |



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# UNITED STATES PATENT OFFICE

# CERTIFICATE OF CORRECTION

Patent No. 3,275,557 September 27, 1966

Ray C. Hughes

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 34, for "tthe" read -- the --; column 4, line 32, for "grm" read -- gram --; line 37, for "obtainer" read -- obtained --; column 5, line 30, for "0.1" read -- 0.2 --.

Signed and sealed this 1st day of August 1967.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents