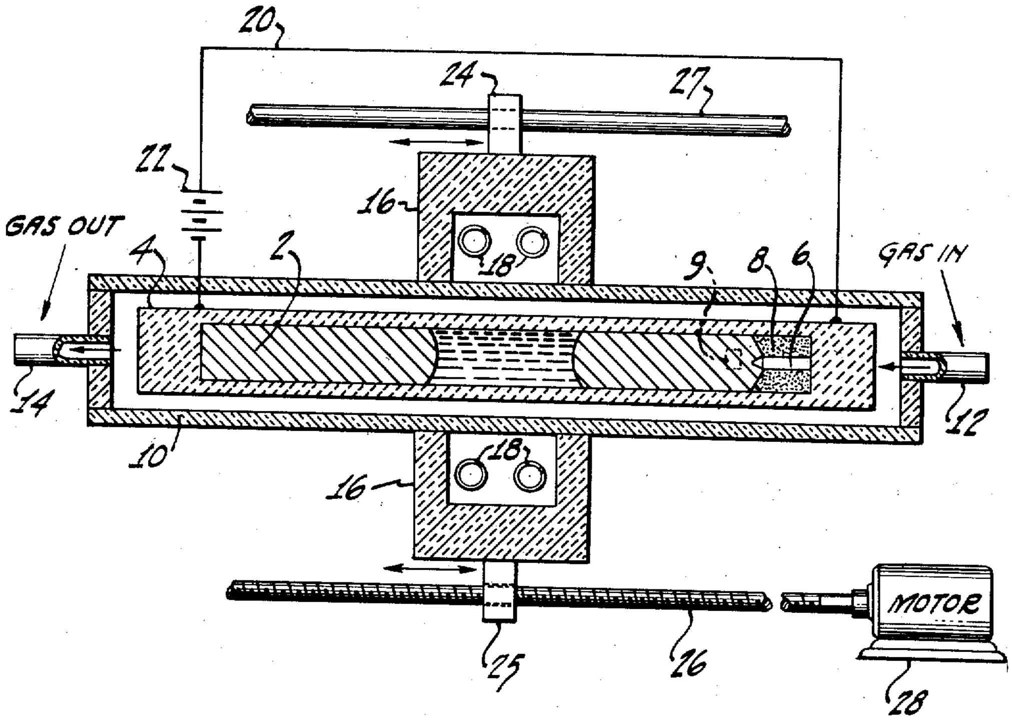
April 16, 1957 R. V. JENSEN 2,789,039

METHOD AND APPARATUS FOR ZONE MELTING

Filed Aug. 25, 1953



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United States Patent Office

2,789,039

Patented Apr. 16, 1957

2,789,039

METHOD AND APPARATUS FOR ZONE MELTING

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Application August 25, 1953, Serial No. 376,404

4 Claims. (Cl. 23—301)

This invention relates to methods and apparatus for zone melting and more particularly to improved methods and apparatus for growing single crystals of materials such as germanium by a zone melting process.

The principles of zone melting are well known. See, for example, an article entitled "Principles of Zone Melting" by W. G. Pfann, in the Journal of Metals for July 1952, page 747. In zone melting a relatively narrow molten zone is caused to traverse the length of an elongated charge of an alloy or a metal. The process has been found advantageous in purifying metals and is especially useful in purifying semi-conductor materials such as germanium. The process is also adaptable to growing a single crystal.

In growing a single crystal ingot by the zone melting technique the shape of the advancing interface between the molten zone and the growing crystal is important. This interface, in order to promote single crystal growth of the ingot, is preferably made convex with respect to the growing crystal. Crystal growth tends to progress in a direction normal to the interface. A convex shaped interface, therefore, provides a freezing front such that undesired non-uniform crystal growths tend to extend toward the outer edges of the ingot and not to continue along the length of the ingot. A concave interface, on the other hand, permits the growth of undesired crystal structures from the outer edges of the crystal toward the center causing non-uniformity of the growing crystal.

Previous methods of growing single crystals by the zone melting process comprise the use of an insulating crucible or boat, usually of silica. The walls of an insulating crucible have a greater thermal resistance than does a metallic charge in the crucible. Therefore, the charge cools by conduction of heat down its length rather than by conduction towards its outer edges. Thus, central portions of the ingot are made to freeze before the outer edges to provide a convex interface.

Insulating crucibles, however, are subject to certain disadvantages which are overcome by the instant invention. They impede the flow of heat from a furnace to the charge in the crucible and tend to lengthen the molten zone. They are usually brittle, easily broken, and difficult to form into accurate shapes. Quartz, for example, cannot be machined, nor can it be readily formed into a crucible having a sharply rectangular cross-sectional shape.

Accordingly it is an object of the invention to provide improved apparatus for zone melting.

Another object is to provide improved methods of zone melting utilizing a thermally conductive crucible.

Another object is to provide improved methods of zone melting utilizing a crucible of a conductive, relatively soft, machinable material.

A further object is to provide an improved method of zone melting suitable for growing single crystals of materials such as germanium.

According to the invention single crystal growth is conducted in a zone melting furnace. A desired convex interface between the growing crystal and the molten zone is provided by utilizing a conductive crucible and heating the walls of the crucible preferably by passing an electric current through them. Thus the outer edges of a charge in the crucible are heated by the crucible walls in addition to the zone furnace heat so that the central portions of the charge freeze first to produce a desired convex interface.

The invention will be described in greater detail with reference to the drawing of which the single figure is a partially schematic, cross-sectional plan view of apparatus according to the invention.

In a preferred embodiment of the invention a single crystal of germanium may be grown utilizing the apparatus shown in the drawing. An ingot **2** of germanium is placed within a carbon crucible **4**. At one end of the crucible a seed crystal **6** is held in position by a mass of silica sand **8**. A desired quantity of an impurity-yielding material (not shown) may be placed in a depression **9** in the ingot near the seed crystal. The impurity-yielding material determines the conductivity of the material, and is so introduced in this process to provide improved uniformity of electrical characteristics throughout the length of the ingot. The crucible is placed within a refractory tube **10** that may be of quartz and is provided with gas inlet and outlet means **12** and **14**. The tube and crucible assembly is surrounded by a zone melting furnace **16** which extends longitudinally along a relatively small portion of the length of the assembly.

The zone furnace may be heated by any convenient means such as the electric resistance heating elements **18** connected to any convenient power source (not shown). The furnace is adapted to travel along the length of the crucible from one end to the other at a controlled rate. Any convenient means may be provided controllably to propel the furnace along the tube. For example, the furnace may be supported by the two brackets **24** and **25** which rest on the rail **27** and the screw **26** respectively. The screw may be rotated by the motor **28** to propel the furnace in a desired direction at a controlled speed. Alternatively, the furnace may be held stationary and the crucible may be adapted to progress through the furnace. Electrical leads **20** are connected to opposite ends of the crucible and to the terminals of the battery **22**, or other power source, to induce a flow of electric current through the walls of the crucible.

In a typical apparatus the crucible **4** may be about 24" long and 1" in diameter, for example, and the germanium ingot may weigh about 1 kilogram. The size of the seed crystal is not critical but it should be large enough so that a portion of it may be melted without melting the entire crystal. In operation, a protective gas such as hydrogen or an inert gas of the zero column of the periodic table is maintained within the tube.

Sufficient electric power is applied to the carbon crucible to heat the crucible and its contents to a temperature about 200° to 300° C. below the melting point of the germanium.

The zone furnace is moved close to the seed crystal end of the crucible and heated. As soon as the zone furnace heat has melted a zone of the ingot about 1" long, the furnace is moved slowly toward the seed crystal until the molten zone includes a portion of the seed crystal. The furnace is then driven back away from the seed crystal toward the opposite end of the crucible at a rate of approximately 1–3 mm. per minute.

The temperature of the molten zone is not critical. It should be substantially higher than the melting point of the ingot material in order to insure complete melting of the entire mass within the molten zone. If the molten zone is maintained at a temperature only slightly above the melting point, relatively small solid crystallites of the material may remain in the molten zone without melting. These crystallites may provide additional nucleating centers as the zone progresses and interfere with the growth of the large single crystal. Generally, any temperature at least about 50° C. above the melting point of the material of the ingot is sufficient to insure complete melting of the zone.

As the furnace is driven along the length of the crucible, a continually changing portion of the ingot is melted and refrozen. In refreezing, the material forms a substantially single crystal structure whose orientation is determined by the seed crystal initially placed at one end of the crucible.

The rate of travel of the furnace is only slightly variable according to the temperature at which the molten zone is maintained. In general, for reasons of economy, it is desirable to move the furnace at approximately the maximum crystal growth rate. If the furnace is moved too rapidly, the freezing ingot will not form a single crystal but will grow in a polycrystalline form. In growing a single crystal of germanium, for instance, a speed of about 1 to 3 mm. per minute gives satisfactory results when the molten zone is maintained about 50° C. above the melting point of germanium. The maximum growing speed also varies according to the orientation of the crystal growth.

Single crystal growth is promoted by the shape of the liquid-solid interface as explained heretofore. For example, discontinuities in the walls of the crucible may provide undesired nucleating centers for the growth of disoriented crystals. Such crystals tend to grow in a direction normal to the crucible walls. While still relatively small, therefore, they meet and stop growing at the advancing boundary of the principal crystal. A convex interface is provided by the resistance heating of the walls of the crucible, which permits freezing to take place primarily by cooling from the ends of the crucible. Thus, heat travels from the outer edges of the newly formed crystal toward the center. The outer edges thus are maintained at a higher temperature than the central portion of the crystal so that the central portion is made to freeze before the outer portion.

When the furnace has traversed the entire length of the crucible, the entire ingot has been converted to a single crystal and the process is complete.

An important feature of the invention is the relatively uniform heating of a charge along its entire length simultaneously with additional heating of a zone portion of the charge. The uniform heating may be conveniently provided by passing an electric current through an electrically conductive crucible. Crucibles made of materials such as carbon or tungsten may be utilized. If the material to be melted is not inert with respect to the material of the crucible an inert liner or boat may be provided chemically to insulate the crucible from the charge. For example, in melting silicon, which is adversely affected by carbon, a silica liner may be provided in a carbon crucible.

It should be understood that the practice of the invention is not limited to heating a conductive crucible by inducing an electric current in it. The instant invention contemplates providing relatively uniform heating of a crucible by any known means such as a gas fired flame or an electric resistance element insulated from the crucible. Such heating is utilized to provide heating of peripheral portions of the ingot so that cooling of the ingot will occur in an outward direction from the central portions thereof.

The method of heating the zone furnace is not critical. Electric resistance elements such as bars of silicon carbide known commercially as Globars are suitable. Furnaces wherein the ingot is heated by induction or by other means such as gas may be substituted for the electric resistance heated furnace.

In zone melting metals such as germanium and silicon it is desirable to provide a protective atmosphere such as hydrogen or an inert gas to prevent oxidation of the heated metal and to minimize the introduction of impurities into the metal. The presence of a special atmosphere is desirable in many zone melting applications. However, the provision of a protective atmosphere is not an essential part of the instant invention and may be omitted in certain instances such as when zone melting chemically stable salts or oxides.

The practice of the instant invention is not limited to the particular materials described heretofore. It is equally applicable to zone melting of other materials, such as metals generally and salts. Neither is the practice of the invention limited to any particular type of zone furnace. Any known means of providing a relatively narrow moving zone of relatively high heat may be utilized.

What is claimed is:

1. A method of zone melting comprising heating an elongated vessel containing a charge of material substantially uniformly along the length of said vessel to a temperature below the melting point of said material, and raising the temperature of a progressively longitudinally changing portion of said charge substantially above its melting point whereby there is produced a convex interface with respect to said molten zone between the molten zone and the adjacent solid matter.

2. A method of growing a single crystal of a material by zone melting comprising placing a seed crystal of said material at one end of an elongated vessel, placing a polycrystalline mass of said material in said vessel adjacent said seed crystal, heating said vessel substantially uniformly along its length to an elevated temperature below the melting point of said material, heating a portion of said material including a portion of said seed crystal to a temperature above said melting point thereby to form a molten zone of said material whereby there is produced a convex interface with respect to said molten zone between the molten zone and the adjacent solid matter, and causing said molten zone to travel along the length of said mass thereby to form a single crystal of said material.

3. Zone melting apparatus comprising an elongated vessel of carbon adapted to hold a molten charge, heating means comprising means for inducing an electric current through the longitudinal walls of said vessel to thereby heat said vessel substantially uniformly along the length of a charge held therein, and means for raising the temperature of a progressively longitudinally changing transverse portion of said charge above the temperature of other portions thereof.

4. Zone-melting apparatus according to claim 3 in which said means for raising the temperature of a portion of said charge comprises a furnace shorter than and substantially surrounding a portion of said vessel, and means for moving said furnace with respect to said vessel along the length of said vessel.

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