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CRYSTAL-GROWING APPARATUS AND METHODS

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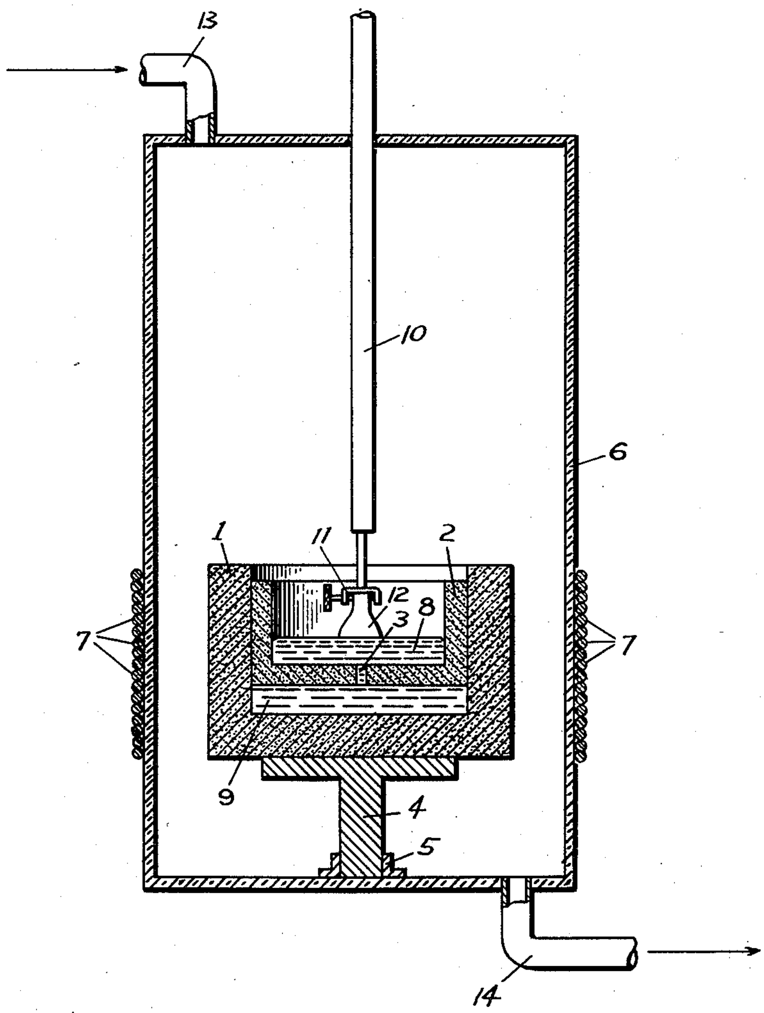

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CRYSTAL-GROWING APPARATUS AND METHODS

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This invention relates to an apparatus and a method used to grow single crystals of uniform electrical resistivity to be employed in the manufacture of transistors and crystal rectifiers, and specifically to the crucible used to obtain such crystals from a melt of semiconductor material.

In the preparation of semiconductor single crystals, the seed-pulling method has been used with considerable success. However, in order that these single crystals may be useful for rectifiers and transistors, the electrical resistivity of the crystal should be uniform throughout its length and the crystal should be readily reproducible. Since several important parameters of transistors vary more or less linearly with the resistivity of the single crystal, the difficulty of making units with predictable characteristics is greatly increased if uniform resistivity is not obtained in the crystal during the growing process.

The change in resistivity along the length of a single crystal may be attributed primarily to the fact that the p-type and n-type doping agents, such as arsenic, antimony, gallium and indium, commonly added to a melt of pure semiconductor material, such as germanium or silicon, are more soluble in the liquid semiconductor material than in the solid semiconductor material. Hence, in a growing crystal, the concentration of doping agent in the solid semiconductor crystal, hereinafter referred to as C_S, is less than the concentration of doping agent in the adjacent liquid semiconductor material, hereinafter referred to as C_L. Therefore, as a crystal is progressively grown by the seed-pulling method, a steadily increasing concentration of doping agent is left in the remaining melt of semiconductor material.

For example, the value of C_s/C_L may vary from 0.001 to 0.1 depending on the doping element used, and for these values of C_s/C_L, C_L is approximately inversely proportional to the volume of liquid semiconductor material remaining in the crucible. Since C_s/C_L remains effectively constant throughout the crystal-growing process, an increased C_L leads to an increasing C_s and since the electrical resistivity of the crystal is inversely proportional to C_s, the resistivity progressively decreases throughout the length of the crystal. For example, in growing a 400-gram crystal of doped germanium from a 500-gram melt, the resistivity may decrease by a factor of four or five along the length of the crystal. Such variations necessitate detailed selection and classification of the slices made from the single crystal material, and this is both wasteful of time and material. Whereas several methods have been proposed to improve this situation, such as precisely varying the crystal-pulling rate, using larger melts of semiconductor material or controlling the rate of solidification, these methods involved complicated procedures and equipment and the chances of growing an impure or imperfect crystal are increased.

This invention relates to means whereby the concentration of doping agent in the liquid semiconductor material, C_L, and the volume of the semiconductor material is kept substantially constant throughout the seed-pulling process

so that a single crystal of uniform resistivity may be grown. In one embodiment of the invention, a pair of cylindrical crucibles, the second of which is designed to fit loosely into the first, is used. The second or inner crucible is provided with a small hole drilled through the bottom thereof. Thus, the crucibles are proportioned so that, when a charge of high purity undoped or lightly doped semiconductor material is melted in the outer crucible, the inner crucible may be placed therein so the bottom thereof rests on the surface of the melt. By pushing down slightly on the inner crucible the melt may be forced through the hole until the inner crucible assumes a position of equilibrium so that it is floating in the melt and contains a portion of the melt therein. A doping agent is then added to the melt in the inner crucible. Thus, the outer crucible contains a melt of lightly doped or undoped semiconductor material and the inner crucible holds a melt of semiconductor material having a substantially greater concentration of doping agent therein.

A single crystal may be grown from the melt described above by the seed-pulling method and, as the crystal grows, the lightly doped semiconductor material will flow from the outer crucible into the inner crucible to maintain the equilibrium level. Therefore, until the inner crucible touches the bottom of the outer crucible, the volume of liquid semiconductor material in the inner crucible will remain exactly constant. Since only a small fraction of the doping agent is used up in the growing crystal C_L remains practically constant throughout the process, and the resistivity of the crystal is uniform. The small decrease in C_L during growth due to the fraction of doping agent used up by the crystal is corrected by lightly doping the entire original melt, as previously mentioned, with a quantity of doping agent equivalent to that used up by the crystal.

With the easily fabricated apparatus described above, large p-type or n-type single crystals having uniform electrical resistivity throughout may be grown. This novel device is easy to operate and the furnace structure used to heat the crucibles and the operation thereof is greatly simplified because the melt is kept at a fixed temperature throughout the growing process. Also, no elaborate equipment for programming the pulling speed is required.

This invention and the features thereof will be understood more clearly and fully from the following detailed description of one embodiment of the invention with reference to the accompanying drawing wherein a schematic view of the crystal-growing apparatus is shown.

Referring now to the drawings, a pair of crucibles **1** and **2** made in accordance with this particular embodiment of the invention is shown mounted within a crystal-growing apparatus. For purposes of illustration, it will be assumed that these crucibles are to be inductively heated and that a germanium single crystal is to be grown. Therefore, the crucibles **1** and **2** should be electrically conductive, thermally responsive to the heating means, chemically inert with respect to germanium and readily heated in a high-frequency field. Crucibles made of high purity graphite fulfill these requirements and have been used successfully for the purposes of this invention. Both of the crucibles shown are cylindrical in shape, and each is provided with a cylindrical recess therein adapted to hold a melt of semiconductor material, in this instance germanium. The inner crucible **2** is designed to fit into the recess in the outer crucible **1** and should be free to move up or down therein. The inner crucible **2** is provided with a small opening **3** extending through the floor thereof. This opening should be so proportioned that, when a crystal of germanium is drawn, as explained below, the diffusion or mixing of the doping agent through the opening 3 to the outer crucible 1 will be undetectable. For example, in a crucible approximately twice the size of the inner crucible 2 shown in the drawing, an opening one-eighth inch in diameter and one-fourth inch long has been used successfully. It should be noted that the size of the crucibles also may be varied according to the density, amount and type of semiconductor material to be melted therein.

The outer crucible 1 may be mounted and supported on a frame 4 which is, in turn, fixed with a flange 5 to the floor of a cylindrical furnace chamber 6. The walls of the chamber 6 may be made of quartz, for example, and are designed to enclose the crystal-growing apparatus. A series of high-frequency induction coils 7 may be disposed around the outside of the chamber 6 in the area adjacent to the crucibles to heat these crucibles sufficiently to melt a charge of germanium to be placed therein. These coils are also used to maintain melt at a predetermined temperature during the crystal-growing process.

The operation of the crystal-growing apparatus may be initiated by first placing a charge of lightly doped germanium in the outer crucible 1 and heating it to about 950 degrees centrigrade or slightly above the melting point of germanium. The inner crucible 2 is then lowered into the recess of the outer crucible 1 and is pushed down against the melt therein so that germanium begins to flow through the opening 3 and into the inner crucible 2. The flow of germanium is continued until the inner crucible has assumed a position of equilibrium. At this stage of the process, the inner crucible should be floating in a germanium melt and should contain a portion of the melt therein, as shown in the drawing. A pellet of doping material, such as a predetermined amount of antimony if an n-type crystal is to be grown, may then be placed in the melt in the inner crucible 2. It should be noted that the doping agent should be the same as that used to slightly dope the entire original melt. Thus, the inner crucible will contain a melt of germanium 8 having a predetermined concentration of doping agent, which has been selected in accordance with the characteristics desired in the finished single crystal, and the outer crucible 1 will contain a slightly doped melt of germanium 9. The amount of doping agent to be used in the original melt is determined by evaluating the quantity of doping material that will be used up by the single crystal during the growing process. For example, in a typical crystal-growing operation, two to three percent of the doping agent is removed from the melt by the crystal. Therefore, the original melt should contain an equivalent amount of doping agent, that is, two to three percent of the amount of doping material used in the pellet. As explained below, this amount will exactly replace the quantity of doping material used up by the crystal.

The actual crystal-growing operation may be commenced by lowering a seed crystal, not shown, which is fixed to a pull rod 10 by a clamp 11, into the melt 8 in the inner crucible 2. The pull rod is then rotated and slowly raised so that a crystal 12 may be started and grown. Thus, as the crystal is slowly grown, the melt 9 in the outer crucible 1 will flow through the opening 3 into the inner crucible 2 to maintain the equilibrium level. Since the volume of the germanium melt 8 in the inner crucible is constant during the growing process and the fraction of doping agent used up in growing the crystal is replaced by the doping agent in the lower melt, C_L remains constant and the electrical resistivity throughout the crystal remains uniform. The process is completed when the lower melt 9 has been exhausted and the inner crucible 2 rests on the floor of the outer crucible 1. It should be noted that, from the time the initial charge is melted until the crystal-growing process is completed, the chamber 6 is continuously flushed with a protective gas, such as argon, for example, to prevent atmospheric contaminants and undesirable reactions from affecting the crystal. Therefore, the chamber 6 is provided with an intake tube 13 and an exhaust tube 14 whereby the protective gas may enter and leave the chamber.

However, it should be understood that this invention is not limited to the particular details described above, as many equivalents will suggest themselves to those skilled in the art. For example, the doping agents and semiconductor materials used and the relative concentrations thereof may be varied as desired. Furthermore, the melt in the outer crucible 1 may be a pure undoped semiconductor material because the volume of the melt in the inner crucible 2 is kept substantially constant during the crystal-growing process, and under these conditions the resistivity of a slightly doped single crystal is negligibly affected by the small decrease in concentration of doping agent in the melt. Likewise, the crucibles 1 and 2 can be resistance heated as well as inductively heated and may be made of materials other than graphite depending upon the chemical and physical properties of the semiconductor material to be melted therein. Therefore, it is desired that the appended claims be given a broad interpretation commensurate with the scope of the invention within the art.

What is claimed is:

1. A crystal-growing apparatus comprising a first container having a recess therein adapted to receive an initial melt of semiconductor material, a second container movably disposed within said recess in said first container and adapted to float in said initial melt, said second container having a recess therein adapted to receive a portion of said initial melt and a predetermined concentration of doping agent, and an opening through a wall thereof, the size of said opening causing the remainder of said initial melt to pass slowly into said second container and preventing said portion therein from effectively diffusing into said remainder, and means for pulling a single crystal from said portion of said initial melt.

2. A crystal-growing apparatus comprising a first container, a second container adapted to float on a melt of semiconductive material in said first container said second container having an opening of such size in a wall thereof that said melt will pass slowly into said second container but will be substantially prevented from passing back into said first container and means for pulling a single crystal of semiconductive material from the melt in said second container.

3. A crystal-growing apparatus comprising a first container adapted to receive an initial melt of semiconductive material having a predetermined concentration of doping agent therein, a second container movably disposed in said first container and adapted to float in said initial melt, means for pulling a single crystal from said second container, and an orifice in the base of said second container of such size as to allow said initial melt to pass slowly into said second container to form a second melt of semiconductive material, but substantially prevent said second melt from passing back into said initial melt, whereby said initial melt is added to said second melt at a rate substantially equal to the rate at which said second melt is removed from said second container to form said crystal during operation of said pulling means.

4. A crystal-growing apparatus comprising a pair of movably nested containers, the outer one of which is adapted to receive an initial melt of semiconductive material having a first predetermined concentration of doping agent therein, and the inner one of which is adapted to float in said initial melt and to receive a second melt of semiconductive material having a second predetermined concentration of doping agent therein, means for pulling a single crystal from said second melt, and an orifice in the base of said inner container of such size as to allow said initial melt to pass slowly into said second melt, but substantially prevent said second melt from passing into said initial melt whereby the concentration of doping agent in said second melt is maintained sub-

stantially constant as said crystal is pulled from said second melt.

5. A crystal-growing apparatus comprising a pair of movably nested containers, the outer one of which is adapted to receive an initial melt of semiconductive material having a first predetermined concentration of doping agent therein, and the inner one of which is adapted to float in said initial melt and to receive a second melt of semiconductive material having a second predetermined concentration of doping agent therein, means for pulling a single crystal from said second melt, an orifice in the base of said inner container of such size as to allow said initial melt to pass slowly into said second melt, but substantially prevent said second melt from passing into said initial melt whereby the concentration of doping agent in said second melt is maintained substantially constant as said crystal is pulled from said second melt, and means for maintaining said initial and said second melts at substantially the same temperature during the operation of said pulling means.

6. A crystal-growing apparatus comprising a pair of movably nested containers, the outer one of which is adapted to receive an initial melt of semiconductive material having a first predetermined concentration of doping agent therein, and the inner one of which is adapted to float in said initial melt and to receive a portion of said initial melt and a second predetermined concentration of doping agent, means for pulling a single crystal from said portion, and an orifice in the base of said inner container of such size as to allow the remainder of said initial melt to pass slowly into said portion at a rate substantially equal to that at which said portion is removed from said inner container to form said crystal, and substantially prevent said portion from passing into said remainder.

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