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Brau et al.

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[54] **ENHANCEMENT OF SOLID STATE RECRYSTALLIZATION BY INDUCED NUCLEATION**

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[52] **U.S. Cl.** ..... **148/1.6,** 148/171, 148/172, 252/62.3 V, 423/508, 23/301 R, 75/169

[51] **Int. Cl.** **B01j 17/02,** H01l 3/20

[58] **Field of Search** ..... 148/1.6; 252/62.3 V; 423/508; 23/301 R; 75/169, 65 ZM

[56] **References Cited**

UNITED STATES PATENTS

1,793,672	2/1931	Bridgman	148/1.6 UX
2,953,690	9/1960	Lawson et al.	75/169 X
3,468,363	9/1969	Parker et al.	75/169 X
3,622,399	11/1971	Johson	148/1.6
3,656,944	4/1972	Brau	75/135
3,723,190	3/1973	Kruse et al.	148/1.6 X

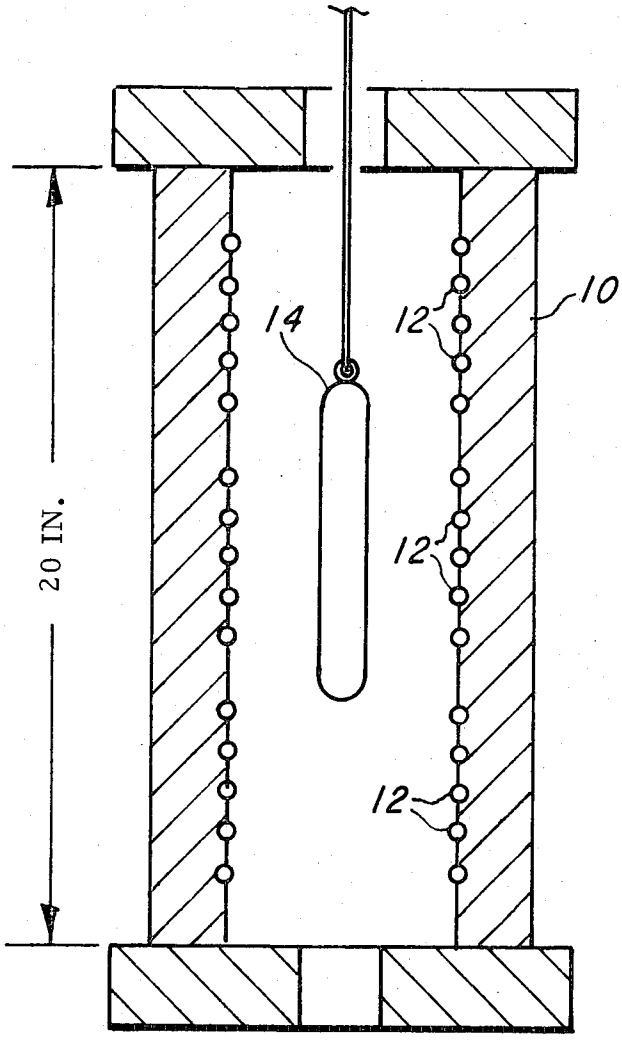
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[57] **ABSTRACT**

A method of forming single crystal semiconducting alloys from polycrystalline material is disclosed. One end of a polycrystalline ingot of a ternary alloy such as (Hg, Cd)Te is melted to cause some crystal growth from the liquid at the liquid-solid interface. The crystal growth forms a seed or nucleation site. The crystal structure is then propagated through the rest of the ingot by any suitable solid state crystal growth technique.

8 Claims, 3 Drawing Figures



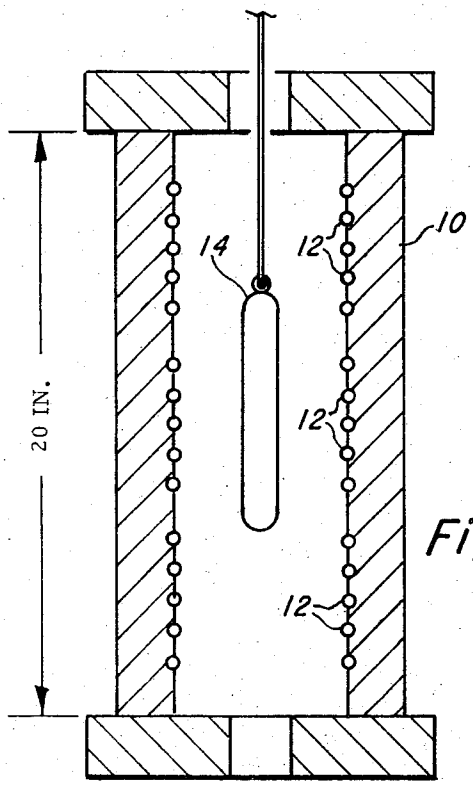


Fig. 1

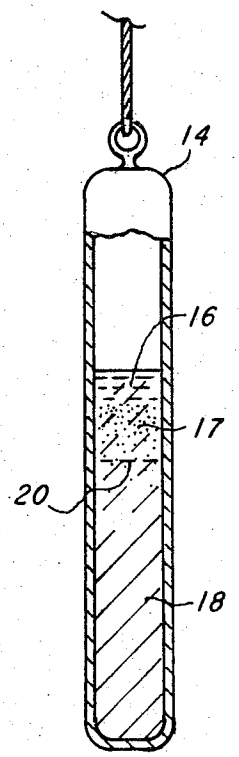


Fig. 2

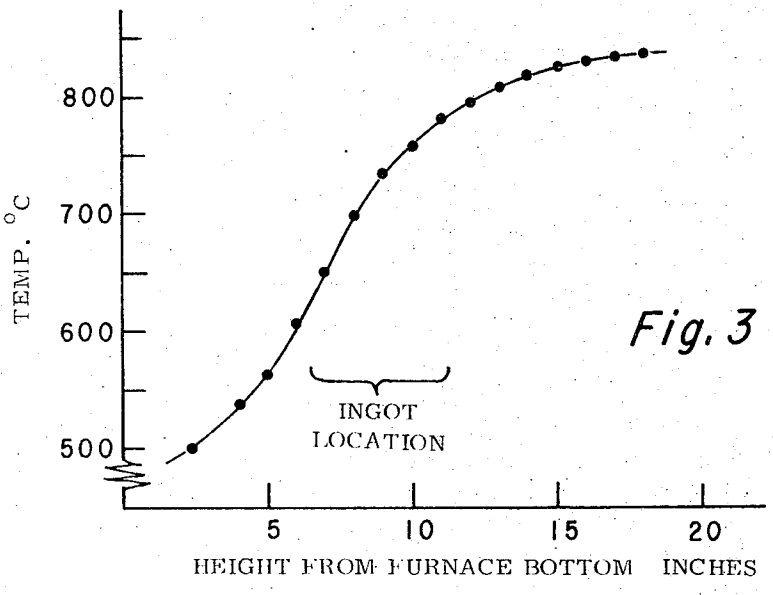


Fig. 3

ENHANCEMENT OF SOLID STATE RECRYSTALLIZATION BY INDUCED NUCLEATION

This invention relates to the production of single crystal tenary semiconductor compounds and more particularly to mercury cadmium telluride ((Hg,Cd)Te) from polycrystalline material.

Mercury cadmium telluride is a ternary alloy which is often described as a pseudo-binary alloy since the mercury and cadmium behave as though they were only one element in combination with the tellurium. This alloy is a highly useful semiconducting material for the manufacture of electromagnetic radiation detectors. The intrinsic band gap of the material varies with the relative amounts of mercury and cadmium present. Accordingly, by varying the composition of the material, the detectable wavelength of the devices fabricated therefrom can be varied over a considerable range. Several methods have been developed for production of homogeneous ingots of this material having a predetermined composition, such as that disclosed in U.S. Pat. No. 3,656,944.

It is desirable that (Hg,Cd)Te material which is to function as a detector be single crystal. A majority of the ingots presently produced are polycrystalline. The use of a Bridgman furnace to produce single crystal from a polycrystalline ingot is discussed in U.S. Pat. No. 3,656,944. This method generates a gradient in the relative mercury and cadmium content from one end of the ingot to the other due to slow melting and refreezing. The result is that only a small portion of the ingot will be of the desired composition even if the entire ingot is a single crystal.

Another method for producing single crystal material from polycrystalline ingots is disclosed by T. C. Harman in the Solid State Research report of the Lincoln Laboratory MIT, 1970 Vol. 3, p. 2. This process involves melting a portion of a polycrystalline homogeneous ingot to form a slush region, that is a mixture of liquid and solid material, between the liquid and solid regions. Mass transfer from the liquid to the slush changes the composition of the slush causing it to freeze and form single crystal material. This method produces single crystal homogeneous material in only a portion of the ingot. The composition of this single crystal portion is also different from the original composition.

Any process for forming single crystal (Hg,Cd)Te in which the material is melted and refrozen results in a change in composition of the material.

Several methods of solid state recrystallization, or annealing of polycrystalline materials are known in the art. Such a process is particularly useful in forming single crystals of ternary alloys such as (Hg,Cd)Te since the material remains solid and no compositional change occurs during crystal growth. Recrystallization generally causes an increase in the crystal grain size throughout the ingot. Growth of one or only a few crystals grains larger than the rest is often termed secondary recrystallization. This large grain growth is the goal when single crystal semiconductor material is needed. A nucleation site or seed is a region of single crystal material which will grow at the expense of other crystal regions in an ingot, and this causes secondary recrystallization. Present recrystallization methods depend upon the natural occurrence of a nucleation site to cause single crystal growth through an ingot. The result is that most recrystallized ingots are not substantially single crystal.

Accordingly, it is an object of the present invention to provide a process for forming single crystal (Hg,Cd)Te material from substantially all of a polycrystalline ingot of (Hg,Cd)Te.

It is also an object of the present invention to provide a process for forming single crystal (Hg,Cd)Te material from polycrystalline (Hg,Cd)Te without changing the relative concentrations of mercury and cadmium.

It is also an object of the present invention to provide a process for enhancement of solid state recrystallization by formation of a single crystal nucleation site.

Briefly stated, this invention consists of the steps of melting a small portion of one end of an ingot of polycrystalline (Hg,Cd)Te to initiate crystal growth from the liquid at the liquid-solid interface and then causing the single crystal structure to propagate through the rest of the ingot by solid state recrystallization. The small amount of crystal growth at the liquid-solid interface acts as a nucleation site for the solid state recrystallization.

Other objects and features of the invention will become more readily understood from the following detailed description and appended claims when read in conjunction with the accompanying drawings, wherein:

FIG. **1** is a cross-sectional view of a zone heating furnace with an ampoule containing an ingot of (Hg,Cd)Te in place;

FIG. **2** is an exploded view of the ampoule in FIG. **1**; and

FIG. **3** is a graph representing a temperature gradient maintained in the furnace of FIG. **1.**

Referring to FIGS. **1** and **2,** a conventional electrically powered resistance-heated zone furnace is composed of an alumina wall **10** which defines a cylindrical chamber and heating elements **12.** Positioned within the chamber is a quartz ampoule **14** containing an ingot of polycrystalline homogeneous (Hg,Cd)Te of the desired composition. The ingot is shown with a small portion **16** in liquid state, a small slush region **17,** and the remainder **18** in solid state.

In operation, the ampoule **14** with the solid ingot is placed in the furnace and a temperature gradient established according to FIG. **3.** The ampoule is positioned such that only a small portion **16** of the (Hg,Cd)Te material is at a temperature above its melting point. The greater portion **18** of the ingot remains in solid state. Since the material was homogeneous when placed in the furnace a region **17** of slush material, that is a mixture of liquid and solid material, will form between the liquid and solid state regions. Mass transfer from the liquid portion **16** to the slush region **17** will change the composition of the material at the edge **20** of the solid material. The change will raise the melting point of this region causing it to freeze and form single crystal material at the interface **20.**

This thin region of single crystal (Hg,Cd)Te grown from the liquid forms a nucleus or seed at one end of the solid region **18.** The ingot is then treated by any standard solid state recrystallization technique to cause the single crystal structure to propagate through the ingot. One such technique is to simply maintain the entire ingot at an elevated temperature, below the melting

point, for a period of time. The difference in free energy of the single crystal nucleus and the rest of the ingot establishes a driving force which allows the single crystal structure to propagate through the solid material **18.**

Another method allows the entire process to be carried out with a single furnace setup and increases the speed of the solid state recrystallization. This technique is to leave the ampoule in the furnace as shown in FIG. **1** after the single crystal nucleus is formed and to maintain a temperature gradient in the furnace as shown in FIG. **3** for a period of time. The temperature gradient thus imposed on the solid region **18** adds an additional driving force to the solid state recrystallization step and increases the rate of single crystal growth.

Since regions **16** and **17** of the ingot were melted in the nucleation step, mass transfer occurred causing the relative concentrations of Hg and Cd to vary through these regions. Therefore even if single crystal structure is formed in regions **16** and **17,** they will be of little value. Region **18** remained solid through the process preventing the occurrence of any mass transfer. The single crystal material formed from region **18** will therefore have the same composition as the original ingot.

For a more complete understanding of the present invention and the method by which it is carried out, the following example is provided. This example is intended only to be illustrative and is not intended to delimit the invention in any manner.

The polycrystalline ingot was prepared according to U.S. Pat. No. 3,656,494 as follows. An approximately 20 cm long quartz ampoule having an inside diameter of 10 mm and outside diameter of 16 mm was cleaned in a conventional manner. The ampoule was then loaded with 38.3795 grams of mercury, 5.7165 grams of cadmium, and 30.9040 grams of tellurium. The ampoule was then sealed and reacted overnight at 800°C. The ampoule was then oil quenched.

The ingot thus formed was approximately 12 centimeters long and had a uniform composition of $Hg_{.790}Cd_{.210}Te_{1.000}$. The ingot was left in the ampoule and placed in a 3 zone furnace with the thermal profile illustrated in FIG. **3.** The ampoule was positioned so that approximately 2 centimeters of the ingot was at a temperature above the melting point of this composition material. These conditions were maintained for 21 days. The ampoule was then removed from the furnace and cooled and the ingot was removed from the ampoule. Upon inspection all the material which remained solid throughout the process was found to be single crystal and homogeneous with the same composition as the originally prepared ingot.

Although the present invention has been shown and illustrated in terms of a specific process, it will be apparent that changes or modifications can be made without departing from the spirit of the invention as defined by the appended claims.

What is claimed is:

1. A method for enhancement of solid state recrystallization of a polycrystalline ternary semiconductor compound consisting of the step of melting a portion of a polycrystalline ternary semiconductor compound ingot and allowing single crystal growth from the liquid to occur at the liquid-solid interface whereby a single crystal mucleus is formed at the liquid-solid interface.

2. A method for enhancement of solid state recrystallization of polycrystalline (Hg,Cd)Te consisting of the step of melting a small portion of a polycrystalline (Hg,Cd)Te ingot and allowing single crystal growth from the liquid to occur at the liquid-solid interface whereby a single crystal nucleus is formed at the liquid-solid interface.

3. A process for forming single crystal (Hg,Cd)Te material from polycrystalline (Hg,Cd)Te material consisting of the steps of creating a nucleus of single crystal material by melting a small portion of a polycrystalline (Hg,Cd)Te ingot whereby single crystal growth occurs at the liquid solid interface and propagating the crystal structrue through the rest of the ingot by solid state recrystallization.

4. A process according to claim **3** including the step of refreezing the melted portion of said ingot after the nucleus is formed at the liquid solid interface.

5. A process according to claim **3** wherein the polycrystalline material is of uniform predetermined composition, so that the single crystal material formed by solid state recrystallization is of the same uniform predetermined composition.

6. A process according to claim **3** wherein the solid state recrystallization step consists of maintaining the ingot at an elevated temperature below the melting point of the material whereby the single crystal structure propagates from the nucleus through the ingot.

7. A process for forming single crystal (Hg,Cd)Te material from polycrystalline (Hg,Cd)Te consisting of the step of maintaining a temperature gradient throughout an ingot of polycrystalline (Hg,Cd)Te such that a small portion of said material is melted at the high temperature end and the temperature continuously decreases to the low temperature end whereby liquid state single crystal growth occurs at the liquid-solid interface forming a nucleation site from which the single crystal structure is propagated through the solid state portion of the ingot.

8. A process according to claim **7** wherein the polycrystalline material is of uniform predetermined composition, so that the single crystal material formed from the portion which remained solid is of the same uniform composition.

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