

[54] **METHOD OF GROWING SINGLE CRYSTALS OF COMPOUNDS**

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[22] Filed: **July 13, 1973**

[21] Appl. No.: **378,818**

[52] U.S. Cl. **23/301 SP; 23/305; 423/111; 23/273 SP**

[51] Int. Cl. **B01j 17/20**

[58] Field of Search **23/301 SP:294, 305, 273 SP; 423/111**

[56] **References Cited**

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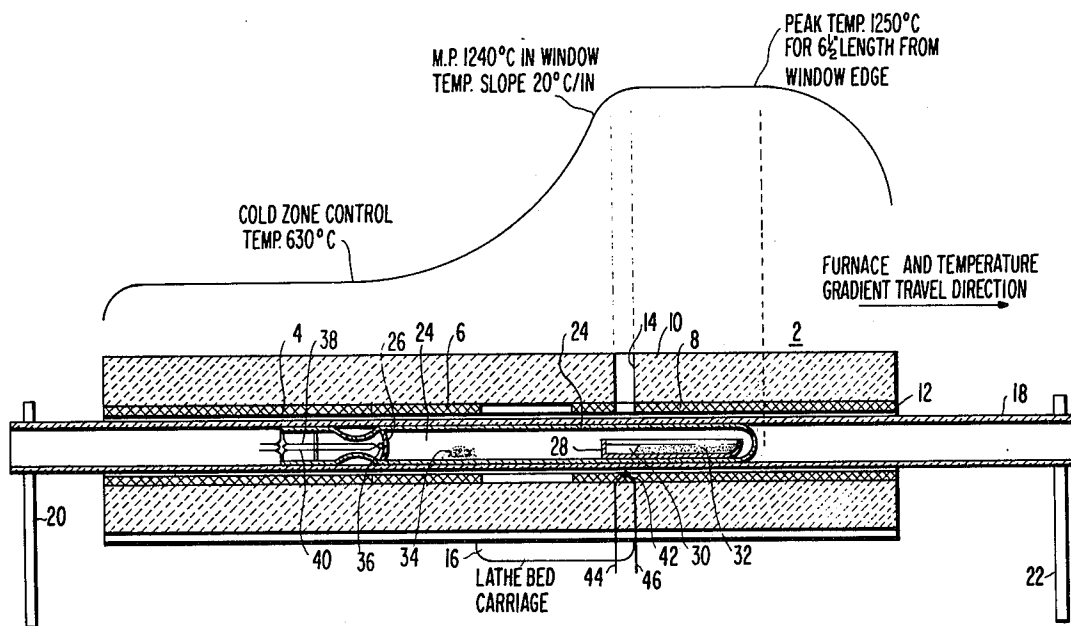
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[57] **ABSTRACT**

In growing a single crystal of a compound or an alloy composed of a plurality of compounds, having a volatile element, from a melt of the compound in a sealed ampoule, a quantity of the volatile element is provided to maintain an atmosphere of the volatile element over the melt and the temperature of the reservoir is slowly cycled around a given temperature, thereby cycling the vapor pressure of the volatile element of single crystal in the product.

3 Claims, 2 Drawing Figures



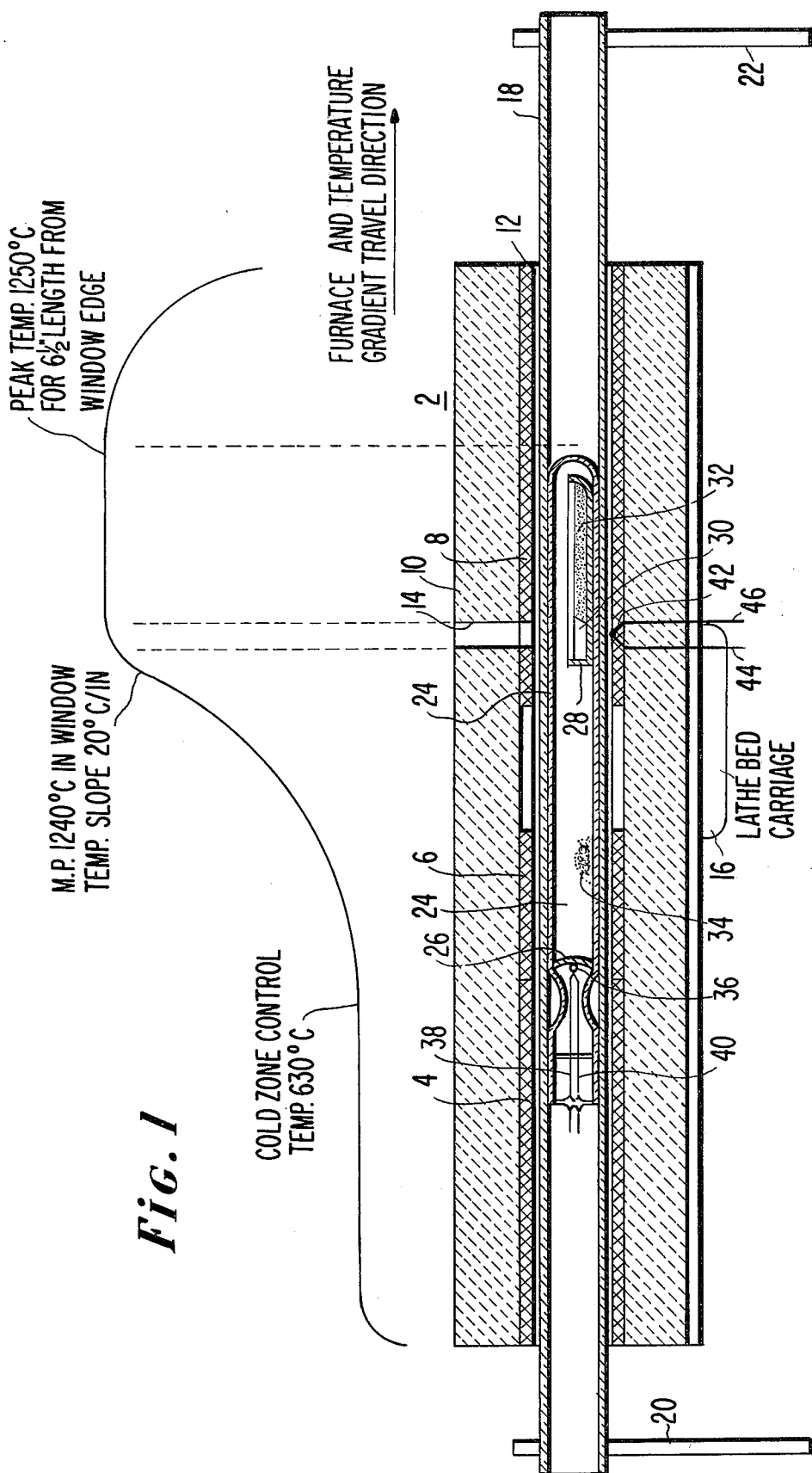


Fig. 1

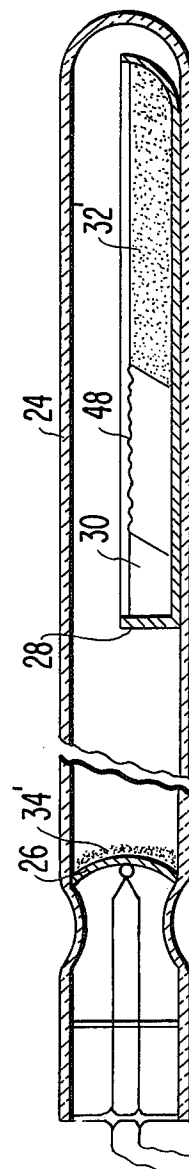


Fig. 2

METHOD OF GROWING SINGLE CRYSTALS OF COMPOUNDS

BACKGROUND OF THE INVENTION

Gallium arsenide single crystals are used for making injection lasers (among other things). This application requires that the crystals be of high quality with a low dislocation density.

Although single crystals of gallium arsenide can be grown by any one of several methods, a method of particular interest is one in which a seed crystal is placed in contact with a melt of gallium arsenide in a boat within a horizontal Bridgman furnace. The boat and a quantity of arsenic are contained within a sealed ampoule. The arsenic is maintained at a temperature cooler than that of the boat containing the seed and the melt but warm enough to maintain arsenic vapor at a pressure of 1 to 1.5 atmospheres over the melt. A crystal is grown by moving the boat and a heat zone with respect to each other so that the melt is progressively frozen beginning at the seed end and progressing toward the opposite end.

In the past, great care was exercised to try to keep the arsenic vapor pressure as constant as possible within the ampoule as the crystal was grown. This was accomplished by keeping the temperature of the arsenic as constant as possible. A sensing thermocouple was disposed adjacent the arsenic and the thermocouple was used to control the current supplied to the zone heater. However, it was found that, despite the great care taken to maintain constant arsenic vapor pressure, single crystal yield has averaged about 50%.

The present invention is based on the discovery that single crystal yield of a compound such as gallium arsenide that contains a relatively volatile component, can be greatly increased by slowly cycling the temperature of the additional quantity of volatile element around a mean temperature, thereby also cycling the volatile element vapor pressure within the ampoule.

THE DRAWING

FIG. 1 is a schematic section view of apparatus that can be used to carry out the method of the present invention, as it appears during a preliminary stage of the method, together with a typical temperature furnace profile for growing a crystal of gallium arsenide, and

FIG. 2 is a somewhat enlarged cross-section view of part of the apparatus shown in FIG. 1, as a crystal is being grown.

DESCRIPTION OF PREFERRED EMBODIMENT

Apparatus, as shown in FIG. 1, may be used to carry out the improved crystal growing method of the present invention. The apparatus may comprise an electrically heated furnace 2 having controlled heating elements for providing a relatively cold zone 4, a zone 6 of intermediate heat and a hot zone 8. The heated zones are surrounded with firebrick insulation 10. The furnace has a central cylindrical chamber 12 extending horizontally from end-to-end.

For convenience in observing the progress of the crystal growth, an observation window 14 extending through the firebrick insulation 10 and the heating coil of the hot zone 8, is provided.

The entire furnace 2 is movably carried on a lathe bed carriage 16 which has means (not shown) for moving the furnace in a steady motion at a controlled rate

along a limited path. The furnace of this example has a length of 36 inches.

Within the central chamber 12 of the furnace 2 is suspended a mullite tube 18 mounted on end supports 20 and 22 which are outside the furnace. The tube 18 has an outer diameter which is slightly less than the inner diameter of the furnace chamber 12 so that the tube 18 and the furnace 2 can move freely with respect to each other.

Within the mullite tube 18 is a quartz ampoule 24. The mouth of the ampoule is closed with a glass seal 26 after the ampoule is loaded as will be described later.

Within the ampoule 24 is a quartz boat 28. To grow a crystal of gallium arsenide, for example, the boat 28 is loaded by placing a seed crystal 30 of gallium arsenide properly oriented at one end of the boat. The rest of the boat 28 is filled with a mass 32 of polycrystalline gallium arsenide. A quantity of arsenic 34 is placed on the bottom of the ampoule 24 between the boat 28 and the cold end of the ampoule (seal 26). After the ampoule 24 is loaded, the ampoule is evacuated to a pressure of about 10^{-5} Torr and closed by means of the glass seal 26. Alternatively, the gallium arsenide can be prepared within the boat by reacting gallium metal and arsenic vapor.

In order to aid in accurately controlling the temperature of the cold zone 4 of the furnace, a thermocouple 36 is provided adjacent the glass seal 26 within the ampoule 24. The thermocouple 36 has lead wires 38 and 40 which are connected to a programmer and current control device (not shown). Another thermocouple 42 is provided within the hot zone 8 to aid in accurately controlling the temperature at the interface between the seed crystal 30 and the liquid melt 32' (FIG. 2) which results from melting the polycrystalline mass 32. The thermocouple 42 has lead wires 44 and 46 connected to a current control device (not shown).

When a crystal is to be grown, the ampoule 24 is disposed within the mullite tube 18 so that the boat 28 is within the hot zone 8 of the furnace 2 and the peak temperature portion of the hot zone extends only to the interface between the seed crystal 30 and the melt 32'. The observation window 14 aids the operator in accurately positioning the ampoule 24 and boat 28. The opposite end of the ampoule containing the arsenic supply 34 must be well within the cold zone 4.

After the ampoule 24 is properly positioned, current is turned on to the three zones 4, 6 and 8 of the furnace 2. The furnace has the temperature profile shown in FIG. 1 of the drawing.

When the furnace 2 has become fully heated, the polycrystalline mass 32 becomes molten. Also some of the arsenic 34 is vaporized and an arsenic atmosphere becomes established throughout the ampoule 24 including the space above the boat 28. Preferably, the arsenic vapor is at a pressure about 1 to 1.5 times normal atmospheric pressure (at sea level). Some of the arsenic supply 34 condenses on the cold wall of the seal 26 to form a deposit 34'.

To grow a crystal, the furnace 2 is moved on the lathe carriage 16 so that the hot zone 8 very slowly (e.g., one-fourth inch per hour) moves away from the seed crystal 30. Successive portions of the melt 32' solidify to form a single crystal 48 attached to the seed 30. Ordinarily, in a process of this type, usable single crystal yield averages only about 50%.

In the improved method of the present invention, the temperature of the cold zone 4 is very slowly cycled in a sinusoidal manner within a range between -1° to $+1^{\circ}$ C and -5° to $+5^{\circ}$ C with respect to the normal mean sublimation temperature of the arsenic. The cycle period is about 10 to 30 minutes. The temperature cycling causes a corresponding cycling of the arsenic vapor pressure.

When crystals are grown by this method, usable single crystal yield approaches 95 - 108% of low-dislocation crystal.

Although the method has been illustrated in growing crystals of gallium arsenide, it applies equally well to growing crystals of other III-V compounds in which one of the elements is so volatile that an atmosphere of the volatile element must be maintained over the melt which is being solidified so that the melt will not become non-stoichiometric due to loss of some of one of the constituents. Examples of other suitable compounds are indium arsenide and gallium phosphide. The method also is not limited to III-V compounds.

The method is also applicable to other crystal growing methods, for example, the vertical Bridgman method, horizontal gradient freeze method, vertical gradient freeze method, and traveling solvent method.

We claim:

1. In a method of growing a single crystal of a III-V compound, one element of which is relatively volatile with respect to another element of the compound, by maintaining a seed crystal of the compound in contact with a melt of the compound within a sealed chamber disposed within a furnace and progressively moving a hot zone relative to said seed and said melt, away from said seed, and in which a quantity of said relatively volatile element is maintained within said sealed chamber adjacent said melt but at a lower mean temperature than that of said melt such that a part of said relatively volatile element becomes vaporized and such that an atmosphere of said relatively volatile element is maintained over said melt, the step of continuously cycling the temperature of said quantity of said volatile element after it has become vaporized, around said mean temperature within a range between -1° to $+1^{\circ}$ C and -5° to $+5^{\circ}$ C, thereby cycling the pressure of said atmosphere, the period of said cycling being about 10 to 30 minutes.

2. A method according to claim 1 in which said compound is gallium arsenide.

3. A method according to claim 1 in which the single crystal is grown in a horizontal Bridgman type furnace.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. 3,877,883

DATED April 15, 1975

INVENTOR(S) Samuel Berkman/Philip Michael Britt

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the "Abstract" change the last two lines to read:

clinging the vapor pressure of the volatile element within the ampoule. This results in a higher percentage of single crystal in the product.

In the specification:

Col. 3, line 10, change "108%" to -- 100% --.

Signed and Sealed this

twenty-second Day of July 1975

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks