July 21, 1970 T. S. PLASKETT ET AL 3,520,810

MANUFACTURE OF SINGLE CRYSTAL SEMICONDUCTORS

Filed Jan. 15, 1968 2 Sheets-Sheet 1

FIG. 1

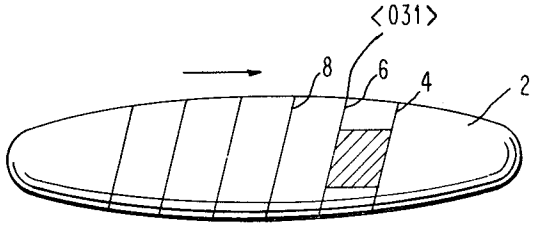



FIG. 2

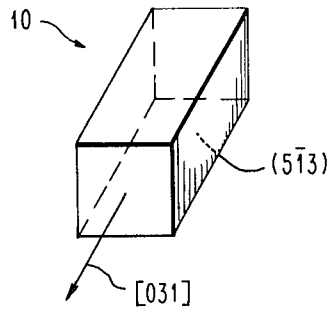



FIG. 3

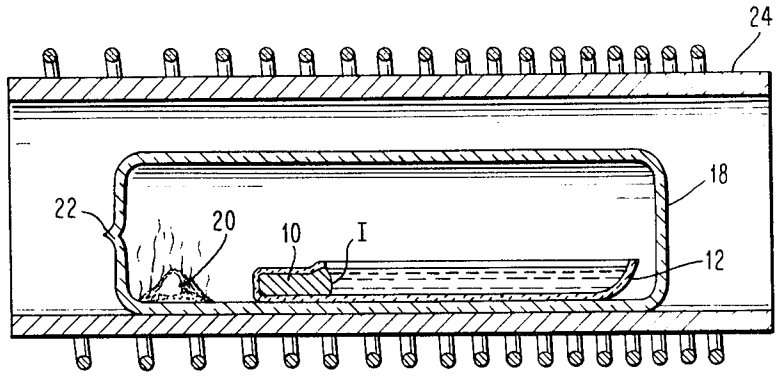
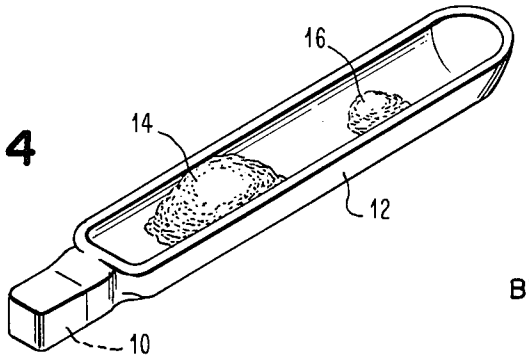



FIG. 4




INVENTORS
THOMAS S. PLASKETT
JERRY M. WOODALL
WILLIAM C. WUESTENHOEFER

BY
ATTORNEY

FIG. 5

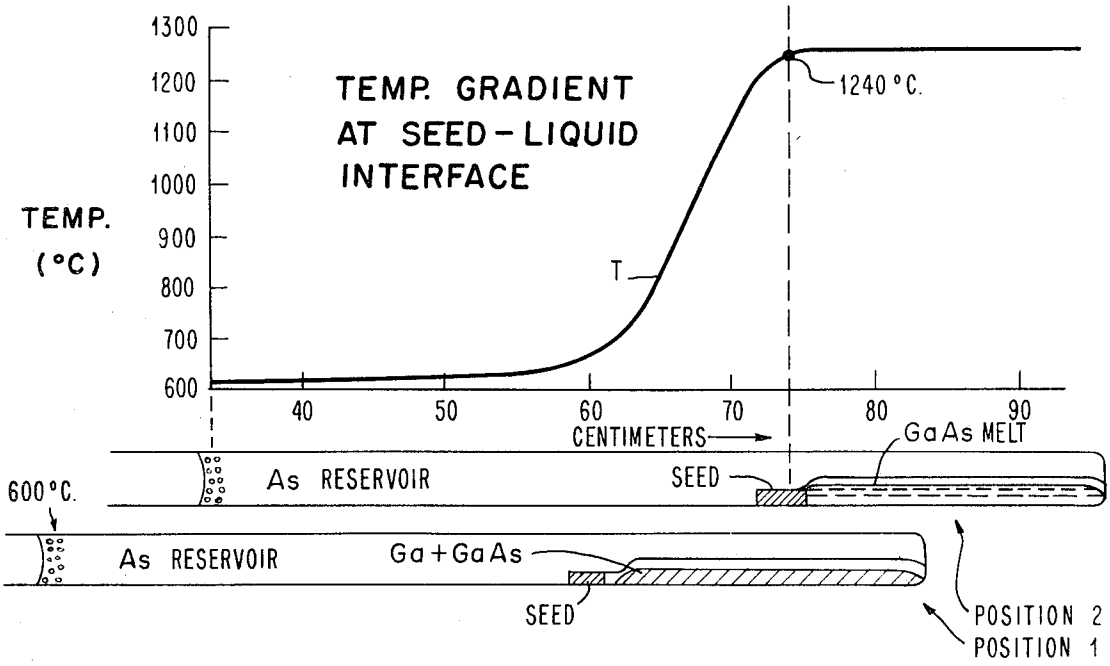



FIG. 6

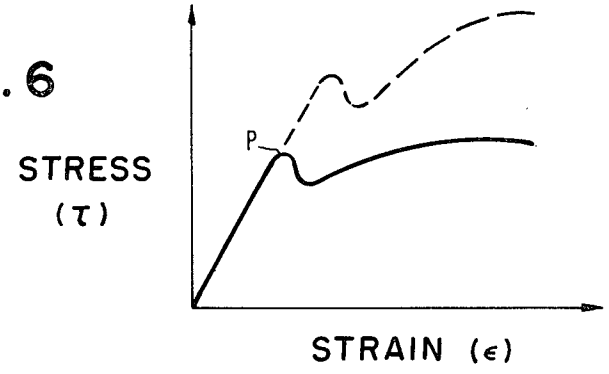
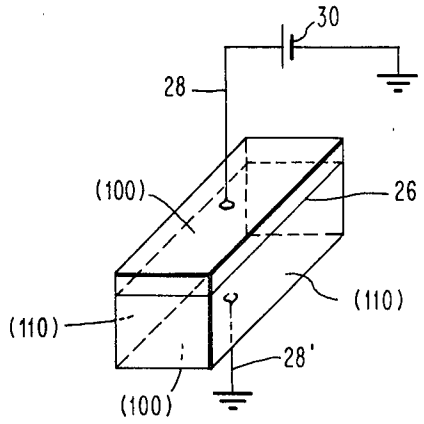



FIG. 7



United States Patent Office 3,520,810
Patented July 21, 1970



3,520,810

# MANUFACTURE OF SINGLE CRYSTAL SEMICONDUCTORS

Thomas S. Plaskett, Ossining, Jerry M. Woodall, White Plains, and William C. Wuestenhoefer, Mahopac, N.Y., assignors to International Business Machines Corporation, Armonk, N.Y., a corporation of New York

Filed Jan. 15, 1968, Ser. No. 697,729
Int. Cl. B01j 17/00, 17/20; H01c 3/00
U.S. Cl. 252—62.3 4 Claims

## ABSTRACT OF THE DISCLOSURE

GaAs injection lasers operate more efficiently and yield higher power outputs if single crystals of GaAs having a high degree of crystalline perfection (free of dislocations and defects resulting from chemical inhomogeneities) are used. For operation as an essential element in an injection laser, the gallium to be combined with the arsenic is heavily doped, such that the resulting GaAs crystal has a carrier concentration of approximately $2–4\times10^{18}$/cc. Previous attempts to grow heavily doped dislocation-free GaAs crystals from a melt by the conventional horizontal Bridgman technique have been unsuccessful. While extreme care has been taken to control pressure and temperature conditions during the growth from a melt of single crystals of GaAs, it was not realized that the dislocation density of a crystal depended on its growth orientation. This disclosure teaches that heavily doped crystals of GaAs grown in the <031> direction are essentially free of dislocations, and that such novel teaching can be applied to the growth of any doped compound provided that the stoichiometry of the compound can be varied and that the growth parameters are maintained under severe control. This disclosures also teaches that dopants with distribution coefficients farthest from unity are preferred for growing crystalline perfect doped crystals. It also teaches that higher As overpressure will enhance crystalline perfection. It further teaches that the stoichiometry of doped crystals changes with growth direction.

## BACKGROUND OF THE INVENTION

It has been ascertained that the power and efficiency of GaAs injection lasers have been increased by the use of GaAs crystals having a very high degree of crystalline perfection. Improved crystalline perfection has been demonstrated in a detailed examination of crystals grown in various crystal orientations in accordance with conventional horizontal Bridgman growing techniques.

It has been known prior to this invention that undoped GaAs crystals have been grown using the Czochralski technique and such crystals can be grown dislocation-free. However, where GaAs has been doped, dislocation occurs in the final crystal and the dislocations increase in number as the doping gets heavier. The present invention is predicated on the discovery that the presence of dislocation defects in doped crystals was found to be dependent upon crystal growth orientation where growth occurred using the horizontal Bridgman technique. It was found that the highest quality crystals are obtained when the GaAs crystals were doped with tin and grown from a GaAs seed oriented along the <031> direction.

While the present invention produces better single doped crystals by growing on a crystal seed whose face lies in an (031) plane, certain other discoveries have made the invention applicable to a wide variety of compounds. By altering the stoichiometry of the GaAs crystal, the high temperature strength of the crystal increases, thus reducing the tendency to generate dislocation during growth. In doped crystals, i.e., where tin is a dopant, such deviations from stoichiometry occur by varying the growth orientation which, in turn, varies the dopant concentration, hence, stoichiometry, in the liquid at the solid-liquid interface. If the As overpressure in the crystal growing system is maintained constant at the dissociation pressure for undoped stoichiometric GaAs, then dopant variation results in a change in the stoichiometry of the growing crystal. Increasing the tin concentration in the melt will increase the number of gallium vacancies in the crystal, so that the stoichiometry of GaAs is not truly one atom of gallium and one atom of arsenic. This alteration changes the physical properties, i.e., it strengthens the GaAs, and maximum strength occurs if growth takes place along the <031> direction.

In general, any doped compound or doped alloy compound of the zinc blende structure can have its stoichiometry altered by growing in the <031> direction.

Further, any undoped compound may have its high temperature strength increased by the addition of materials to the melt which do not alter the chemical identity of the crystal.

It is an object of this invention to grow dislocation-free single crystals of GaAs.

It is yet another object to grow dislocation-free doped GaAs.

A further object is to make dislocation-free GaAs crystals that can be used in the manufacture of injection lasers.

Yet another object is the adding of a material to the melt so that the only effect is to change the stoichiometry of the crystal.

The foregoing and other objects, features and advantages of the invention will be apparent from the following more particular description of a preferred embodiment of the invention, as illustrated in the accompanying drawings.

## BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 shows a completed growth of monocrystalline GaAs in the form of an ignot.

FIG. 2 is a showing of the axis along which said ingots are cut.

FIG. 3 is a showing of a furnace and its contents for growing pure single crystals of doped GaAs.

FIG. 4 is a showing of the quartz boat and its contents.

FIG. 5 is a plot of temperature versus furnace depth during the growth of such crystals.

FIG. 6 is a plot of stress v. strain for a material.

FIG. 7 is a showing of the injection laser made in accordance with the teaching of this invention.

Prior to describing the invention, certain conventions that crystallographers use will be defined. A number commonly called a Miller index surrounded by { } i.e., {100}, indicates a family of planes in a cubic crystal equivalent to the plane in such brackets. A number in parenthese, i.e. (100), indicates a specific plane in a cubic crystal, namely, the 100 plane and no other. The symbol <100> represents a family of directions indicating any and all directions corresponding to cube edges whereas the symbol [100] designates a specific direction, namely, the 100 cube edge. In most of what follows, crystal growth takes plate in the {031} plane along the <031> direction.

## DESCRIPTION OF THE PREFERRED EMBODIMENT

Apparatus for growing single crystal elements and compounds by the temperature gradient freeze process is set forth in U.S. Pat. No. 3,242,075 to D. H. Harris, which issued Mar. 22, 1966. In such patent, one method disclosed comprises placing polycrystalline GaAs in a crucible, melting the polycrystalline material in the cru-

cible, then placing the crucible in a tubular furnace which is capable of producing a temperature gradient along its length so that the crucible is hotter at one end than at the other end. As the temperature of the furnace is reduced, and the gradient is shifted, a portion of the material within the crucible located in the cooler portion of the furnace will freeze, causing a solid-liquid interface. When the gradient has shifted to a point below the freezing point of the material, a single crystal structure is formed. In the Harris patent, it was found that by the judicious use of heat-conducting and heat-insulating shields about the entire length of the crystal, one could maintain the application of substantially linear heat along the entire length of the crystal and thus obtain uniform temperatures at the liquid-solid interface of the crystal as it is being pulled through the furnace. Such uniformity of heat application aided in obtaining growth of nominally uniform single crystals of GaAs. In such Harris patent, however, no mention is made of growing pure single crystals that contain dopants, nor is there any mention of growth along the <031> axis.

In FIG. 1, there is shown a completed ingot **2** of single crystal GaAs grown by conventional methods, i.e., Czochralski technique or horizontal Bridgman technique. The arrow in FIG. 1 indicates the general direction of growth, namely, from left to right of the ingot **2**. The ingot **2** was in a heated boat in a furnace, and as the boat was pulled out of the furnace, a portion of the melt solidified, leaving a solid-liquid interface, growth of the single crystals taking place at the interface.

By placing the ingot **2** on a goniometer and taking Laue photographs, using X-rays, of the crystal, such photographs being well known to crystallographers and not essential to the description of the invention shown and described herein, one is able to locate the <031> axis. he ingot **2** is suitably marked with lines **4**, **6**, **8**, etc. that indicate the orientation of the <031> axis and the ingot is cut along these lines.

In FIG. 2 is shown a block **10** that is cut from ingot **2** having two parallel faces that lie in the <031> plane. Growing of single crystals of heavily doped gallium arsenide takes place in one of these faces in a direction that is perpendicular to the face. This block **10** serves as a GaAs seed onto which dislocation-free single crystals of heavily doped GaAs crystals are grown.

As seen in FIGS. 3 and 4, a quartz boat **12**, whose interior was sandblasted to prevent wetting by any molten material placed therein, contains 40 gms. of gallium **14** and 1.3 gms. of tin **16**. The seed **10** is placed in the left portion of boat **12** with its face (the one lying in the <031> plane) pointing in the direction of the contents of gallium **14** and tin **16** in the boat **12**. While it is not absolutely necessary, very favorable results occur if the horizontal plane of the seed is parallel to a {531} plane at the same time that growth takes place along the <031> direction. The {531} plane must be compatible with the condition that the horizontal plane be perpendicular to the {031} growth planes. For a specific growth direction [031], the compatible specific horizontal plane is $(5\bar{1}3)$. The boat **12** and its contents are placed in a quartz ampoule **18** and 50 gms. of arsenic **20** are placed in a section of ampoule **18**, not in contact with boat **12**. The ampoule is pumped down to a pressure of $10^{-5}$ Torr., and sealed at a point, such as tip **22**; the sealed ampoule **18** is inserted into a furnace **24**, similar to the one shown and described in the above noted Harris patent, but any other furnace equivalent in operation to the Harris furnace and which is used for crystal growing can be employed.

As seen in FIG. 5, the quartz ampoule **18** is loaded into a furnace **24** wherein the reservoir of arsenic remains in the relatively cool portion of the furnace and is heated to 600° C. The boat **12** and its contents are placed in position #1 where the Ga and tin are heated to 1240° C., but the seed is kept in the vicinity of 700° C. The ampoule is kept in this first position for approximately 20 minutes, permitting the Ga melt to react to become a GaAs melt and reach equilibrium and also to prevent the seed **10** from being melted by the unsaturated gallium. The arsenic is kept at ~1 atmosphere and such pressure is closely controlled by maintaining the temperature of a cold spot in the arsenic region of the ampoule to within ±0.5° C., which effectively is the equivalent to a variation in As pressure of about ±0.5 atmosphere.

After the 20 minute interval, the ampoule **18** is inserted further into the furnace at the rate of 5 cm. per hour until it rests in position **2** of the FIG. 5. During the last 2.5 cm. of travel, the As reservoir temperature is raised to 616° C. where it is maintained for approximately 16 hours. During this period, the melt is being further saturated with arsenic and a solid-liquid interface I (see FIG. 3) at equilibrium exists between the seed **10** and the melt. After the 2.5 hour period has terminated the melt is allowed to stand for ½ hour to assure proper seeding, at which time the melt is pulled out of the furnace through the temperature gradient shown by curve T. The melt is pulled through this gradient at the rate of ~0.85 cm./hr. after which time it is removed from the furnace to cool the room temperature.

For this representative seeding procedure using 40 gms. of gallium, 50 gms. of arsensic, 1.3 gms. of tin, the quartz boat was ~14 cm. long and the holder for the gallium arsenide seed **10** was ~2.54 cm. long and 1.1 cm. deep. The quartz ampoule **18** was approximately 90 cm. long.

After the GaAs crystal, grown on the {031} plane of seed **10**, has been removed from the furnace and is cooled, a p-n junction 26 is formed, using conventional P-type dopants, such as zinc. Then the unit is diced along the (110) planes and cleaved along (110) planes perpendicular to the diced (110) plane. GaAs, when cleaved along its (110) planes, results in perfectly parallel faces. Electrodes 28 and 28′ are connected to the two (100) faces that are perpendicular to the (110) planes and the unit of FIG. 7 is now ready to be connected to a suitable source of power, such as battery 30, and be used as an injection laser. Since growth of heavily doped GaAs has taken place in the <031>direction, the GaAs has a particularly low dislocation density, and the latter characteristic makes the GaAs crystal well suited for use in an injection laser, increasing the efficiency and power output of the laser.

For purposes of practicing the invention, a semiconductor is considered heavily doped if the dopant has concentrations between $10^{17}$ to $10^{19}$ holes or electrons/cc. While the invention has been described with respect to doped gallium arsenside, it is to be understood that crystal growth in the <031> direction is applicable for III–V compounds other than GaAs, such as GaP, or for heavily doped compounds of the II–VI groups, such as PbTe, PbS, ZnS, of the Periodic Table, particularly where the stoichiometry of the melts of the doped compounds are controlled by the vapor pressure of one of the elements of the compound. Phosphorus, arsenic, and sulfur are examples of such components which are used to control melt stoichiometry.

Furthermore, the addition of a noncontaminating component to the liquid during crystal growing should effectively change the stoichiometry of the crystal. A noncontaminating component is one which goes into the solid crystal at a level that is less than $10^{16}$ atoms/cc. and thus does not alter the electrical properties of the completed solid crystal. Also, by increasing the As overpressure in the crystal growing phase, one may alter the stoichiometry in the desired direction.

In FIG. 6 is shown a typical plot of stress $\tau$v. strain $\epsilon$ for a material. As stress is applied to a material, the latter will elongate, and so long as the yield point P is not reached, when the strain is removed, the material returns to its original unstressed position at the origin of the

$\tau$V. $\epsilon$ plot. However, should the stress be applied beyond point P, the elastic limit of the material, the latter is permanently deformed. By changing the stoichiometry of the doped GaAs by growing the doped crystal along the <031> axis, the strain v. stress curve is now depicted by the dotted line. In effect, the high temperature strength of the crystal during growth is increased. So long as growth direction is that the distribution coefficient (the stresses are uniaxial, the benefits accuring from off stoichiometric growth and judicious choice of growth axis are obtained.

The reason for choosing the <031> direction as the growth direction is that the distribution coefficient (the ratio of the tin concentration in the solid to that in the liquid) is dependent on the crystal growth direction. From crystal growth theory, it is known that if the distribution coefficient is less than unity, then the liquid layer ahead of the advancing solid-liquid interface is enriched in tin (or any other dopant). The farther the distribution coefficient is from unity the greater is the concentration of tin in this layer, and this occurs in the <031>direction.

If the As overpressure in the crystal growing system is maintained at the dissociation pressure of undoped stoichiometric GaAs, then the addition of tin causes the liquid to increase in As concentration and thus changes the stoichiometry of the growing crystal. The greater the tin concentration in this layer the further the deviation from stoichiometry and the stronger the crystal. The maximum strengths occur near the <031> direction.

The crystalline perfection of any doped compound with one component volatile can be enhanced if the axis of growth is judiciously chosen. The correct axis is determined by knowing the dependence of the distribution coefficient with growth orientation. The axis with the distribution coefficient farthest from unity is required. For the zinc blende structure the <031> is the desirable direction.

It has been shown that dislocation density is related to orientation of crystal growth, with the lowest dislocation density occurring for crystals grown in the <031> direction. Other orientations during growth influence high temperature plasticity of the crystal. The amount of alteration in the ratio between Ga and As due to the presence of tin at the solid-liquid interface during growth of the crystal appears to be dependent on crystallographic orientation. Thus the impurity or dopant concentration profile immediately ahead of the advancing solid-liquid interface is a good measure of the off stoichiometry being produced in the final frozen crystal, and such off stoichiometry strengthens the crystal and makes it less susceptible to dislocation damage at high temperatures. Thus, preferred



growth directions for compound semiconductors that are heavily doped can be more readily determined.

Throughout the above discussion, it should be clear that along the <031>direction, means substantially along that direction and the invention can be practiced even if the growth orientation deviates approximately five degrees around an <031> axis.

What is claimed is:

1. A method of growing a tin doped single crystal of GaAs by the horizontal Bridgman technique comprising:
providing a single crystal seed of GaAs,
contacting the seed to a melt of GaAs so as to provide a solid-liquid interface between said seed and melt,
adding tin to said melt to vary the stoichiometry of the grown crystal, and
growing a GaAs single crystal from said melt along the <031> direction of said single crystal seed.

2. A method for growing a tin doped single crystal of GaAs compound by the horizontal Bridgman technique comprising:
providing a single, crystal seed of GaAs,
cutting said seed along the (031) plane,
contacting said seed at such (031) plane to a melt of GaAs to provide a liquid-solid interface,
providing a dopant of tin for said melt during crystal growth wherein the distribution coefficient of said dopant is less than unity, and growing a single crystal of GaAs along the <031> axis of said single crystal seed.

3. In a method for growing a tin doped single crystal of GaAs compound by the horizontal Bridgman technique starting from a single crystal seed of GaAs, the improvement consisting of
growing a GaAs single crystal from a melt of tin containing GaAs off-stoichiometrically along the <031> axis of said crystal seed.

4. A GaAs injection laser wherein a component of said laser is GaAs single crystal containing $10^{17}$ to $10^{19}$ atoms of tin per cc. of GaAs, grown from a tin containing GaAs melt along the <031> direction of a single crystal seed of GaAs.

**References Cited**

UNITED STATES PATENTS

3,245,847 4/1966 Pizzarello ..... 252—62.3 X

TOBIAS E. LEVOW, Primary Examiner

J. COOPER, Assistant Examiner

U.S. Cl. X.R.

148—172; 23—301, 305; 330—4.3; 331—94.5