

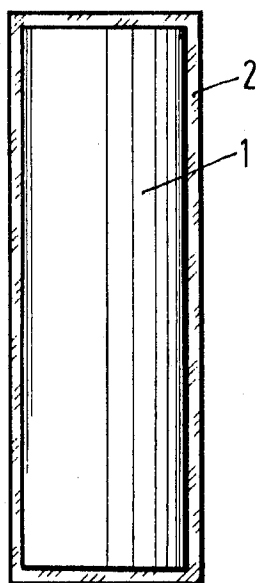
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INCAPSULATING A SEED CRYSTAL FOR PRODUCING MONOCRYSTALS

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1

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## ENCAPSULATING A SEED CRYSTAL FOR PRODUCING MONOCRYSTALS

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6 Claims

### ABSTRACT OF THE DISCLOSURE

Described is a method of producing monocrystals from semiconducting compounds which dissociate at the melting point, preferably gallium arsenide monocrystals. The semiconductor material molten in a crucible is completely encapsulated by a thin layer of boron oxide ( $B_2O_3$ ). The crystal is pulled in accordance with the Czochralski method from the semiconductor melt, with the aid of a seed crystal. The seed crystal according to the invention, to prevent the evaporation of the more volatile component of the semiconducting compound therefrom, is encased, prior to being installed into the pulling device, with a thin film of  $B_2O_3$ .

Our invention relates to a method of producing monocrystals, preferably gallium arsenide monocrystals, from semiconducting compounds which dissociate at their melting point. The semiconductor material is melted in a crucible, totally encapsulated by a thin layer of boron oxide ( $B_2O_3$ ) and is pulled from the semiconductor melt using a seed crystal in accordance with the Czochralski method to yield a monocrystal.

The semiconductor compounds, for example the  $A^{III}B^V$  compounds, supplement and enlarge the number of semiconductor materials available over semiconductor materials such as germanium and silicon. The technical processes for the production of semiconductor compounds with a considerable vapor pressure, that is which dissociate readily at the melting point, such as compounds containing arsenic, still have many shortcomings. Many methods have been employed to produce, purify and grow monocrystals of semiconducting compounds and many theories have been developed in connection therewith.

A method is described in the book "Semiconductor Problems" V, pages 52 and following, wherein a specific equilibrium vapor pressure of the molten compound is maintained in the melting vessel by maintaining a bottom body of the more volatile component, such as arsenic, in the melting crucible, during the solidification process. The same book describes another method wherein the vapor pressure is not regulated by a bottom body but by weighing the components. Another possibility for producing compounds which easily dissociate at the melting point is to employ sub-stoichiometric conditions of the components, meaning that, as in the first-described method, a bottom body is employed whereby the melt is not quite stoichiometric, but that, for example, during the production of gallium arsenide the gallium is present, for example in several percent excess.

The same problems which occur during the production of semiconducting compounds also occur during their monocrystalline growth. Here, the aforementioned methods are appropriately modified. The starting point for monocrystalline growth for semiconducting compounds is the Czochralski method, particularly in connection with producing gallium arsenide. The difficulty consists in keeping all sides of a completely sealed chamber at a high temperature. In the interior of said chamber the seed is to be

2

moved. The easily volatile component of the compound, such as arsenic in gallium arsenide, unless special precautions are utilized, evaporates from the melt and precipitates at the cold places of the melting vessel.

This evaporation may be prevented by melting the compound in a sealed vessel and by maintaining all surfaces which are adjacent to the vaporization chamber, at a temperature above the condensation or sublimation temperature of the more easily volatile component. However, the pulling of the crystal is made more difficult since the pulling movement must now be transmitted into the sealed vessel, while all parts of the vessel are kept at a relatively high temperature. The problem can be solved by using a magnetic system which allows moving the seed. Even employing these quite complicated technical processes, one still cannot prevent the formation of a thick coating of the semiconducting compound on the inside surface of the quartz vessel. During melting processes of longer duration, this coating results in a considerable impairment of permeability (transparency).

Another method, described in "Journal of Phys. Chem. Solids," vol. 26, pp. 782-784, is the so-called encapsulating technique. In this simpler method, the gallium arsenide crystals are free of heavy metal and are, therefore, particularly suitable for specific semiconductor devices, such as gallium arsenide diodes used for very high frequencies, that is the so-called Gunn diodes. The characteristic feature of this method is that a semiconductor material, e.g. of an  $A^{III}B^V$  compound, is melted in a quartz crucible and completely encapsulated by a thin film of  $B_2O_3$ , and then coated by a thicker layer (about 10 mm.) of  $B_2O_3$ . The viscosity of the  $B_2O_3$  melt and the excess pressure which prevails in the vicinity of the melt in a protective gas atmosphere, e.g. argon, at about 1 atmosphere gauge results in preventing dissociation of the hot, or molten, gallium arsenide and evaporation of the arsenic. If, according to the Czochralski method, a gallium arsenic seed, produced in the usual way, is dipped into the  $B_2O_3$  melt and subsequently into the semiconductor melt, the seed above the  $B_2O_3$  melt is heated to such a degree that the dissociation of gallium arsenide at the seed cannot be avoided. This results in the following two difficulties:

(1) The arsenic evaporating from the seed, among other things, coats the viewing windows and clouds the  $B_2O_3$  melt making pulling the crystal very difficult.

(2) The no longer bound, metallic, precipitating gallium collects at the seed and runs into the melt, accumulates at the most concave growth front and disturbs the crystallization of the gallium arsenide.

It is the object of the present invention to eliminate these shortcomings and to devise a method which makes it possible to produce monocrystals from semiconducting compounds which dissociate at the melting point, particularly gallium arsenide monocrystals, by crystallizing from a melt of the same composition.

According to our invention, the evaporation of the more volatile component of the semiconducting compound from the seed crystal is prevented by encasing the seed crystal, prior to its installation into the crystal pulling device, with a thin film, in the order of 500  $\mu\text{m.}$ , of  $B_2O_3$ .

In a further development of our invention, this is preferably effected by immersing the seed crystal into a  $B_2O_3$  melt, heated to approximately 1000° C., for at least about five minutes. The immersed crystal subsequently is pulled from the  $B_2O_3$  melt with a velocity of approximately 10 centimeters/hour. The layer thickness of  $B_2O_3$  is preferably 250  $\mu\text{m.}$

For the purpose of obtaining a better adherence, the seed crystal encapsulated with the  $B_2O_3$  film is tempered immediately following the immersing process, for about five hours, at a temperature between 400 and 800° C. In order to prevent indiffusion of contaminations from the

3

surroundings, it is preferred that both the immersion process and the tempering process be carried out in a protective gas atmosphere, preferably in an argon atmosphere.

Since  $B_2O_3$  has the ability to getter metal oxides and since furthermore the dipping of the crystal seed into the  $B_2O_3$  melt helps to remove, in a simple way, the contaminations which are still present at the surface, our invention is particularly suitable for the production of monocrystals comprised of gallium arsenide, which can be further processed for highest frequency use as, for example, Gunn diodes.

The drawing shows a seed crystal produced in accordance with the invention.

In the drawing, the seed crystal results from the simple immersion of a gallium arsenide crystal 1, suspended by a high melting metal wire, into an anhydrous  $B_2O_3$  melt heated to about  $1000^\circ C.$ , and a slow pulling of the crystal from the melt (about 10 cm./hr.) after an immersion of about five minutes. The crystal becomes immediately surrounded with a mirror-smooth, transparent and clear  $B_2O_3$  layer 2 of approximately 250  $\mu m.$  thickness which completely prevents the evaporation of the easily volatile component and makes the crystal seed usable for any desired number of pulling processes. Prior to its first use, the encased crystal is suspended above the hot melt, in a temperature range between 400 and  $800^\circ C.$  and preferably in an argon atmosphere, for about five hours. This results in a better adherence of the  $B_2O_3$  layer.

We claim:

1. A process for the manufacture of a monocrystal of an  $A^{III}B^V$  semiconductor compound, which decomposes at

4

the melting point, in which the semiconductor material melted in a crucible is completely enclosed by a thin layer of boron oxide ( $B_2O_3$ ) and the monocrystal is drawn from the semiconductor melt in accordance with the Czochralski method by means of a seed crystal, wherein the seed crystal is completely covered with a film on the order of magnitude of 500  $\mu m.$  of  $B_2O_3$  before its introduction in the crucible by immersion in a  $B_2O_3$  melt of  $1000^\circ C.$  and withdrawn from the  $B_2O_3$  melt at a rate of approximately 10 cm./h.

2. The method of claim 1 wherein the immersion is for at least five minutes.

3. The method of claim 2, wherein the  $B_2O_3$  layer produced is 250  $\mu m.$  thick.

4. The process of claim 1, wherein the semiconductor compound is gallium arsenide.

5. The process of claim 4, wherein the covered seed crystal is subjected to a tempering process for approximately five hours, at between 400 and  $800^\circ C.$  in a protective gas atmosphere.

6. The process of claim 5, wherein the protective gas is argon.

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