Description

Background of the invention

Field of the invention

The present invention relates to a method of growth of an inorganic compound single crystal and a boat used for the method. More particularly, the present invention relates to a method for producing, at a high yield, a single crystalline inorganic compound of a IIIb group element(s) and a Vb group element(s) of the Periodic Table by means of a boat growth method. The inorganic compound(s) of a IIIb group element(s) and a Vb group element(s) is hereinafter referred to as an inorganic compound(s).

Description of the prior art

Single crystalline inorganic compounds, such as GaAs, or the like, are produced in most cases by means of the boat growth method. The inorganic compound is melted and then solidified by the gradient freeze (GF) method or the horizontal Bridgeman (HB) method, using a boat. The boat has a semicircular or oval cross section and is made of quartz.

It is known to roughen the inner surface of the boat by means of sand-blasting or the like so as to prevent the inner surface from being wetted by the melt of the inorganic compound. The sand blasting is carried out with finely divided alumina, SiC, or similar powder. If wetting occurs, the silicon of the boat is incorporated into the single crystalline inorganic compound and twins and grain boundaries are generated during growth, thereby lessening the yield of the single crystalline inorganic compound.

The known roughening method is, however, not very effective for preventing wetting in the case of producing a single crystal having a large cross section since the amount of charged melt is great and tends to wet the inner surface of the boat. The known boat growth method involves a difficulty in producing a single crystalline inorganic compound at a high yield.

Summary of the invention

It is an object of the present invention to provide a growth method for a single crystalline inorganic compound by using a boat, which method enhances the yield of such compound.

It is another object of the present invention to provide a boat used in the method mentioned above.

The present inventors studied how to enhance the yield of a single crystalline inorganic compound in the boat growth method. In one of the trials, the present inventors subjected the boat to α-crystobalitizing and used the boat with the white converted quartz powder on the inner surface thereof. The boat could effectively prevent wetting. Nevertheless, the high temperature of more than 1500°C necessary for converting the quartz to α-crystobalite and the long conversion time make the conversion impractical.

After studies and trials, the present inventors discovered that by roughening and tridymitizing the inner surface of the boat at least where contacted by the melt the above-mentioned objects can be attained.

The boat growth method provided in accordance with the present invention is characterized by using a quartz boat having a roughened inner surface, the quartz of the boat being tridymitized on at least the surface of the boat contacted by the melt.

The quartz boat according to the present invention is subjected to roughening for example using SiC, Al_2O_3 or other powder. Roughening herein should be construed under the terminology of the boat growth method to mean the formation of minute indentations on the inner surface of a quartz boat for lessening wetting.

When the trydimitizing occurs, whitening of the boat surface is observed, and the trydimitizing can be verified by an index or powder X-ray photography.

An embodiment of the trydimitizing method is now described.

The roughened quartz boat is pickled and rinsed with water to clean the inner surface thereof. The cleaned quartz boat is dried and then heated to a temperature between a quartz-tridymite transformation temperature, i.e., 830°C, and a tridymite-crystobalite transformation temperature, i.e., 1450°C. A preferred heating temperature is from 900°C to 1200°C. The holding time in the heating temperature is at least 1 hour, preferably at least 2 hours. A long holding time is not particularly inconvenient. The holding time is preferably 10 hours at the longest in the light of operation efficiency and economy. The heating can be carried out in air. The heating for trydimitizing can be carried out in such a manner that finally no quartz of the boat is exposed at the surface of the boat, that is, at least the whole surface of the boat is trydimitized.

The quartz boat subjected to the heat treatment for trydimitizing at least the surface thereof is used for the growth of the inorganic compounds, such as GaAs, GaP, InAs, InSb, InP, and the like. Preferred inorganic compounds to be grown by the boat method according to the present invention are GaAs, InAs, and others having a low vapor pressure, as they are in the known methods.

An embodiment of the boat growth method according to the present invention is explained with reference to the drawings, illustrating the GF method, although the invented method can be applied to the HB method.

Brief description of the drawings

Figure 1 is a longitudinal cross-sectional view of an apparatus for producing a single crystal by the GF method.

Figure 2 illustrates the variation of the temperature distribution in the GF method.

Figure 3 schematically illustrates a cross section of a quartz boat.

Referring to Fig. 1, the quartz boat 1 is disposed

in an ampoule 2 and has, at its right hand end in the drawing, a stepped portion 1a for locating a seed crystal for the growth of a single crystal.

The inner surface 1b of the boat 1 is roughened by sand-blasting or the like. The ampoule 2 is usually made of quartz and consists of a section where the boat 1 is contained and a section where the component including the Vb group element, such as As, is contained. These sections are separated from each other by a partition 3 having a capillary tube 3a. The component including the Vb group element is denoted by reference numeral 4 (hereinafter referred to as the Vb group element 4) and is, for example, As powder. The Vb group element 4 is vaporized and exerts a pressure, which is equal to the dissociation pressure of the inorganic compound at a temperature in the vicinity of the melting point of inorganic compound, on the melt being single crystallized, thereby preventing the vaporization of the Vb group element from the melt and hence quality deterioration of the single crystal.

The electric furnance 5 creates the temperature distribution as shown in Fig. 2. In order to create the temperature distribution, the electric furnace 5 has heating sections 5(1)—5(4) which are sequence-controlled independently from each other.

The electric furnace 6 is used for heating the Vb group element 4 so as to generate the vapor pressure of the As or the like required for preventing dissociation of the inorganic compound. The vapor generated flows through the capillary tube 3a and enters the section where the boat 1 is contained. In a case where the inorganic compound is GaAs, an As vapor of 10^5 Pa (1 atm) is generated by heating to approximately 610°C.

The heat-homogenizing tube 7 protects the ampoule 2 from external and incidental force and smoothens the temperature distribution.

A predetermined amount of the inorganic compound polycrystals required for forming an inorganic compound ingot is placed in the boat 1. Alternatively, the IIIb group element, such as Ga or the like, is contained in the boat 1, and the Vb group element, such as As, in a stoichiometric amount, is not contained in the boat 1 but is supplied by the As vapour or the like. In this case, the Vb group element 4 is in such an amount that it provides the stoichiometric As as well as the vapor pressure for preventing dissociation of the inorganic compound.

The temperature gradient as shown in Fig. 2 is explained. In Fig. 2, the ordinate indicates the temperature by an optional scale while the abscissa indicates, by an optional scale, the distance from one end of the boat 8, where a seed crystal is placed, to the other end of the boat 8. The boat 8 and the abscissa are shown in Fig. 2 by the identical scale. The origin of the abscissa corresponds, therefore, to the starting point of growth, which advances in the direction of the abscissa. The M.P. of the ordinate indicates the melting point of the inorganic compound.

The temperature distribution varies with the time as shown by curves 9, 10, and 11. In curve 9, the temperature of one end of the boat 8, where the seed crystal is placed, is slightly lower than the M.P. while the temperature of the other end of the boat 8 is higher than the M.P., by approximately 20°C—100°C. In curves 10 and 11, the profile of the temperature distribution is maintained as in curve 9 and the cooling is performed at a predetermined cooling rate of, for example, from 0.1°C/hr to 10°C/hr.

In the HB method (not illustrated in the drawings), the temperature distribution is maintained constant, and the electric furnace is mechanically displaced relative to the ampoule or vice versa.

The boat 1 (fig. 3) has an inner surface 1c which has been roughened and tridymitized as shown by 1d, thereby preventing wetting of the inner surface 1c due to the melt 12 which is in contact with the boat surface. The single crystalline inorganic compound can therefore be produced at a high yield and a high purity. In addition, the EPD (etch-pit density) of the single crystalline inorganic compound is low.

The present invention is further explained by way of an example.

Example

(Heat treatment of quartz boat)

The boat used was made of quartz and had a seimcircular cross section 53 mm in diameter and a total length of 300 mm. The inner surface of the boat was roughened by sand blasting with alumina powder (<48 μm, −300 mesh). The boat was then cleaned with acid and water and subsequently dried. The boat was inserted into the electric furnace and heated up to a temperature of 950°C. A temperature of from 900°C to 950°C was maintained for 3 hours, followed by lowering of the temperature.

(Growth of a GaAs single crystal)

GaAs polycrystals in an amount of 1670 g were contained in the boat, which was heat-treated as described above. The seed crystal was a GaAs single crystal having a <111> As surface for seeding growth in the <111> direction. The difference in temperature between the ends of the boat was 70°C, and the temperature of the end of the boat where the seed crystal was placed was 1235°C. The cooling rate was 0.5°C/hr.

The yield of the single crystal was 73% by weight based on the total weight of the ingot produced. The inner surface of the boat did not exhibit wetting at all. The single crystal exhibited an EPD of 3500/cm^2 and a Si concentration of 10^{16}/cm^3 or less.

The above-described growth procedure of a GaAs single crystal was repeated ten times. In each growth procedure, the yield of the single crystal was 70% or higher.

Comparative Example

The same procedure as in the Example was carried out except that the quartz boat was not subject to the heat treatment. In the production of

a GaAs single crystal, wetting was generated on a part of the boat 60 mm to 130 mm distant from the seed crystal. The yield of the single crystal was 28%, the EPD was 85000/cm^2, and the Si concentration was 10^{17}/cm^3.

Claims

1. A method of growth of an inorganic compound single crystal, consisting of a IIIb group element and a Vb group element of the Periodic Table, in which a melt of said inorganic compound is single-crystallized in a boat made of quartz whose inner surface has been roughened at least where contacted by the melt, chracterized in that the growth of the single crystal is performed while said melt is in contact with said inner surface of the boat which has been tridymitized at least where contacted by the melt.

2. A method according to claim 1, wherein said boat has been heated to a temperature of from 830°C to 1200°C for tridymitizing.

3. A boat for use in growing an inorganic compound single crystal, consisting of a IIIb group element and a Vb group element of the Periodic Table, by a boat growth method, the inner surface of the boat having been roughened, characterized in that at least the surface of the boat which the melt of the inorganic compound, in use, contacts has heen tridymitized.

Patentansprüche

1. Verfahren zum Züchten von Einkristallen aus anorganischen Verbindungen, bestehend aus einem Element der Gruppe III und einem Element der Gruppe V des Periodensystems, wobei die Schmelze dieser anorganischen Verbindung in einem Quarzschiffchen, dessen innere Oberfläche zumindest in dem Bereich aufgerauht ist, der in Kontakt mit der Schmelze ist, zu einem Einkristall auskristallisiert wird, dadurch gekennzeichnet, daß das Waschstum des Einkristalls vollzogen wird, während die Schmelze in Kontakt mit der inneren Oberfläche des Schiffchens ist, dessen Oberfläche zumindest in dem Bereich, in dem sie in Kontakt mit der Schmelze ist, tridymitisiert ist.

2. Verfahren nach Anspruch 1, wobei das Schiffchen zum Tridymitisieren auf eine Temperatur von 830°C bis 1200°C erhitzt worden ist.

3. Schiffchen zur Verwendung zum Züchten von Einkristallen aus anorganischen Verbindungen, bestehend aus einem Element der Gruppe III und einem Element der Gruppe V des Periodensystems, durch ein Zuchtverfahren mittels Schiffchen, wobei die innere Oberfläche des Schiffchens aufgerauht ist, dadurch gekennzeichnet, daß zumindest der Bereich der Oberfläche des Schiffchens, den die Schmelze der anorganischen Verbindung bei der Verwendung berührt, tridymitisiert ist.

Revendications

1. Procédé de croissance d'un monocristal de composé inorganique, constitué d'un élément du groupe IIIb et d'un élément du groupe Vb de la Classification Périodique, dans lequel une masse en fusion dudit composé inorganique est transformée ne monocristal dans un creuset en quartz dont la surface interne a été rendue reugueuse au moins aux endroits où elle est en contact avec la masse en fusion, caractérisé en ce que la croissance du monocristal est effectuée alors que ladite masse en fusion est au contact de ladite surface interne du creuset qui a été transformée en tridymite au moins aux endroits où elle est en contact avec la masse en fusion.

2. Procédé selon la revendication 1, dans lequel ledit creuset a été chaufffé à une température allant de 830°C à 1200°C pour réaliser la transformation en tridymite.

3. Creuset utilisable pour la croissance d'un monocristal de composé inorganique, constitué d'un élément du groupe IIIb et d'un élément du groupe Vb de la Classsification Périodique, par le procédé de croissance en creuset, la surface interne du creuset ayant été rendue rugueuse, caractérisé par le fait qu'au moins la surface du creuset qui, pendant l'utilisation, est au contact de la masse en fusion du composé inorganique, a été transformée en tridymite.

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2. A method according to claim 1, wherein said boat has been heated to a temperature of from 830°C to 1200°C for tridymitizing.

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