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H. WELKER ET AL

2,933,384

METHOD OF MELTING COMPOUNDS WITHOUT DECOMPOSITION

Filed Sept. 15, 1954

2 Sheets-Sheet 1

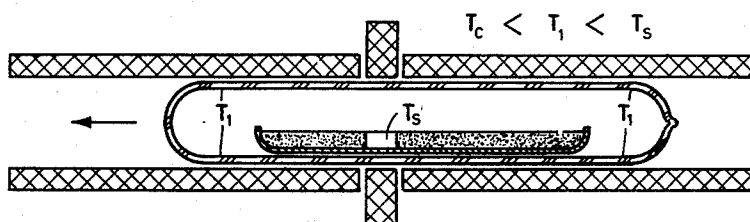


Fig. 1

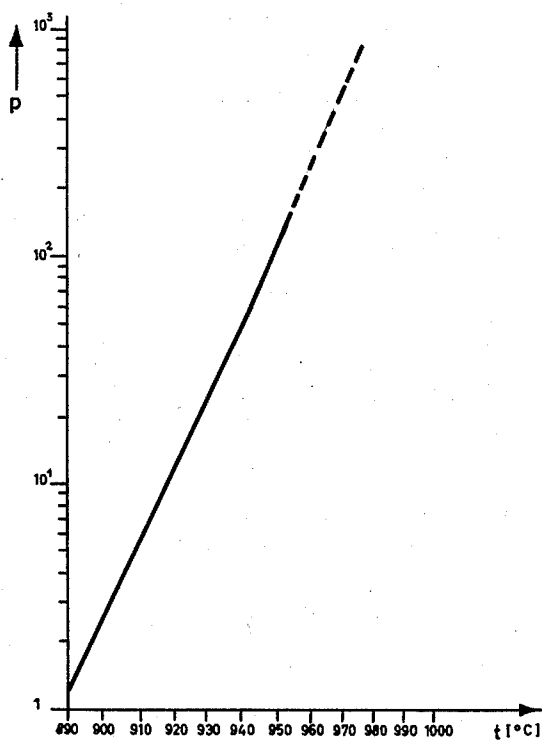


Fig. 2

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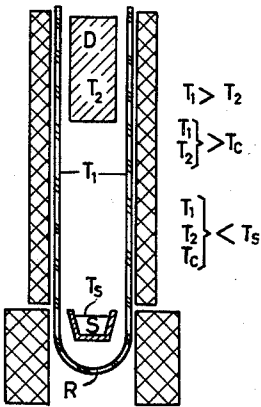


Fig. 4

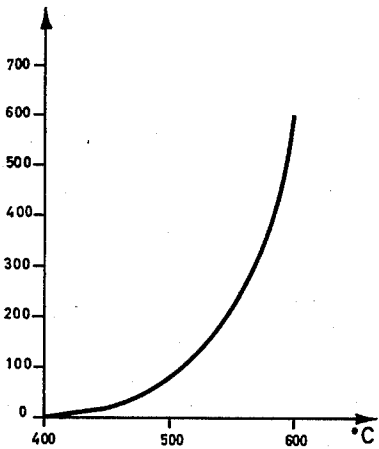


Fig. 3

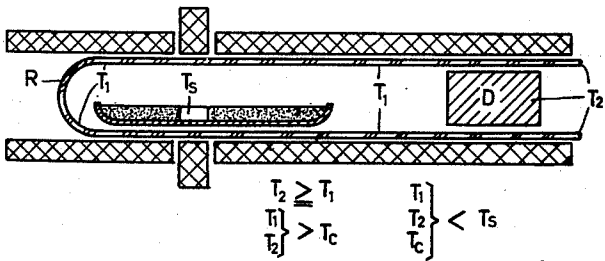


Fig. 5

1

2,933,384

METHOD OF MELTING COMPOUNDS WITHOUT DECOMPOSITION

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11 Claims. (Cl. 75—65)

Our invention relates to a method for melting compounds, particularly semi-conductor compounds, without decomposition. For some industrial purposes, various compounds must be remelted without thereby impairing the accuracy, for example the stoichiometric ratio, of their composition. Electrical semi-conductor compounds, in particular, require a well defined composition, especially from the stoichiometric point of view, whose accuracy must go far beyond the limits of the usual chemical or spectroscopical analyses. In order to obtain properly developed semiconductor crystals of definitely predetermined electrical properties, appropriate semiconductive compounds are subjected, in general, to a melting process serving to obtain, for example, a crystal of the compound from the melt either by means of a zone melting process or by pulling the crystal from the melt.

The terms "zone melting" and "crystal pulling" have well-defined meanings in this art. They are defined in Pfann Patent U.S. 2,739,088; Journal of Metals, pages 747-754, July 1952; and in Transistors: Theory and Applications, by Coblenz and Owens, McGraw-Hill, 1955, pages 77, 78, and 203. In zone melting an ingot of the semiconductor is melted and the molten region moved slowly from left to right along the bar. The impurities generally remain in the liquid phase and are swept along with the molten zone. In crystal pulling the purified semiconductor is melted in a crucible, for example, and into this melt a seed crystal of the semiconductor is dipped, and then slowly withdrawn. The molten material adheres to it and solidifies, to form large single crystals. Obviously, when applying such melting process to semiconductive elements such as silicon or germanium, the melting proceeds without any decomposition of the elementary material. However, the danger of decomposition arises when the process is applied to semiconductor compounds. Decomposition in such cases occurs, generally, because of fractional evaporation of one or several of the components of the melt, resulting a gradual change of the ratio of the individual components. The terms component or components signify the component element or elements of the compound. The term "evaporation" in this connection means the "net evaporation," i.e. the "total evaporation" minus the vapors which, in the course of the melting process, diffuse back into the melt or return thereto as condensate. The compound indium arsenide (InAs), for example, is very stable in the solid state. However, if it is melted without special precautions, arsenic (As) evaporates continuously and the melt becomes progressively poorer in As. Upon solidification, an InAs composition is obtained which, because of excessive In, contains elementary In in form of microscopical inclusions within an InAs matrix. As a rule, such inclusions make the material useless as a semiconductor. It will be understood by persons skilled in this field that indium arsenide is exemplary of a class of electrical semiconductor compounds known to the art.

2

Reference may be had to the report of Von H. Welker in Zeitschrift Naturforschung, August 1952, pp. 744-759, in this relation.

In order to reduce such decompositions, the proposal has been made to perform the remelting processes in enclosed vessels and to heat the vessel walls to the temperature of the melt. This method, however, leaves much to be desired because difficulties due to the high vessel temperature are encountered, for instance, at the sealing and junction points.

It is an object of our invention to eliminate such deficiencies.

More specifically, it is an object of the invention to afford remelting such compounds without decomposition in melting vessels whose temperature, for the most part, is below the melting temperature of the compound. The term "melting vessel," used in this connection, is to designate not only the melting crucible as such, but also the parts immediately connected therewith, in as far as they may exert any influence upon the melting process. Thus, the term "melting vessel" includes the enclosed space about the crucible (which may be filled with an inert gas or may be evacuated), the elements of the device which form the enclosed space, conduit means passing through the enclosed space, throttling means inserted within part of the enclosed space, etc.; but the term "melting vessel" is not to include any parts which are sufficiently far from the melting crucible so as to be without influence upon the process.

The foregoing and other objects, advantages and features of the invention will be apparent from the following description of the methods and devices illustrated by the accompanying drawings, in which:

Fig. 1 shows the construction of an enclosed melting tube;

Fig. 2 is a graph relating to the partial vapor pressure of arsenic over a melt of an indium arsenide;

Fig. 3 is a graph relating to the vapor pressure of arsenic;

Fig. 4 is a schematic view of one embodiment of an open melting tube provided with throttling means; and

Fig. 5 is a schematic view of another embodiment of an open melting tube provided with throttling means.

The essence of the invention consists in retaining certain parts of the melting vessel at a temperature below the melting temperature of the compound being processed. More specifically, the temperature of such parts is kept below the melting temperature and above the condensation temperature of the most volatile component of the compound. In this connection, the term "condensation temperature" is to signify the lowest temperature at which, under the given condition, no condensation will as yet occur, for example, at the walls of the vessel. This condensation temperature is, among other things, a function of the partial vapor pressure of the component in question, this partial vapor pressure being dependent upon the temperature of the molten compound. These conditions determine the lowest temperature permissible to still avoid condensation of the components of the compound at the walls of the vessel. Consequently, evaporation of components from the melt ceases as soon as the partial pressures of the components are in equilibrium with the melt. The process according to the invention, therefore, does not impair the evaporation of the compound as a whole, but it eliminates the influence of any partial evaporation and thus prevents affecting the composition of the melt.

The preferred embodiments of the invention are summarized as follows:

The compound is placed into a substantially enclosed melting vessel providing a vapor space about the compound, heating that part of the melting vessel closest to

the compound to a temperature causing at least a portion of the compound to melt, and as to the remaining part exposed to the vapors, maintaining the coldest spot at a temperature below the melting temperature of the compound but above the condensation temperature of the more readily volatilizable component of the compound.

The process according to the invention may be readily carried out by means of an enclosed melting vessel such as comprising, for example, a closed quartz tube. Fig. 1 shows an embodiment which is particularly useful for zone melting. However, other remelting processes, such as the pulling of crystals, particularly single crystals (see G. K. Teal et al., *Phys. Rev.* 78, 1950, p. 647), or the melting and "normal freezing" (see W. G. Pfann, *J. of Metals*, 1952, pp. 747-753), can also be carried out by means of this and the other embodiments set forth.

Provided the vapor pressure of the composition as well as the vapor pressures of the individual components are known as a function of the temperature, the lowest temperature at which most of the device may be kept is readily established from the fact that at this temperature the vapor pressure over the condensed, solid or fluid component which evaporates most readily is at least equal to the vapor pressure of this component over the melt of the compound, assuming, of course, that the compound is maintained at least at melting temperature.

The compound InAs may serve as an illustration. InAs melts at about 936° C. As shown in Fig. 2, the vapor pressure of As over the molten compound is about 40 mm. Hg. According to Fig. 3, the vapor pressure of As is 40 mm. at a temperature of 485° C. Consequently, no part of the melting vessel should have a temperature below 485° C.

It should be added, however, that, depending upon the experimental condition, the temperature limit determined in this manner may vary in both directions; it will be lower if the surface properties of the melting vessel impede the formation of condensation nuclei of the most readily evaporating component of the molten compound. This is the case when vessels of extremely pure quartz are used. On the other hand, the temperature limit will rise in cases of a relatively high chemical affinity between the vapor of the component in question and the walls of the melting vessel.

Retaining parts of the melting vessel at temperatures below the melting point of the compound has the advantage that, during a remelting process, the compound may be present in the liquid as well as in the solid phase, without any danger of condensation occurring at the solid fraction of the compound. This affords shifting the interface between the solid and liquid portion according to a predetermined schedule, which is important not only in the zone-melting method, but also in pulling crystals from the melt, particularly single crystals. From a technological point of view the employment of temperatures below the melting temperature is advantageous in case of enclosed vessels in view of the fact that any joints or seals of the device may be held at substantially lower temperatures. For example, it is found particularly convenient to keep a ground seal made from quartz at 485° C. instead of 936° C., as in the case of InAs.

The heating of certain parts of the melting vessel to temperatures which, on the one hand, are below the melting point of the compound but, on the other hand, are above the condensation temperature of the components, permits the remelting of compounds without decomposition in open melting vessels, even if advantage is to be taken of the so-called separating tube effect. An arrangement of this type is shown in Fig. 4. S is a crucible, containing the melt, which is heated above the melting temperature T_s . The crucible S is located in a tube R, which may be a quartz tube, heated to a temperature T_1 ($T_1 > T_s$; T_c being the condensation temperature of the component which condenses most readily). D is a plug, retained at a temperature $T_2 > T_c$, which, to-

gether with the surrounding quartz tube, form a throttle for the evolving gases. If, in addition, $T_1 > T_2$ and the quartz tube is arranged vertically, the so-called separating tube effect occurs, i.e. due to convection, the rising vapors of the aforesaid component are returned, so that no net evaporation past the throttling can take place. Within the throttling space, a circulating current develops which, in the present example, travels upward along the inner wall of the tube, and downward along the throttling plug. As to the designing of the tubes and calibration of the throttling bodies in relation thereto, reference is made to the papers of L. Waldmann on the separating tube effect in separating isotopes, *Naturwiss.* 27, 230 (1939), and 29, 467 (1941).

For purposes of this invention, it is often sufficient to throttle without a separating tube effect, as illustrated in Fig. 5. The throttling effect is increased in this case by heating the throttle to a temperature higher than the coldest part of the vessel.

The term "decompose" in the sense of the present invention means that the melt of the particular compound within an inert atmosphere or in vacuum will become depleted of at least one component due to evaporation. The prerequisite for the applicability of the method is that, in the state of equilibrium, the partial vapor pressure of at least one component above the melt is considerably higher than the partial vapor pressure of the remaining component, or components, so that the equilibrium vapor phase consists essentially only of the low volatile component, or components.

We claim:

1. The method of melting with minimized decomposition a compound which exhibits substantially different partial vapor pressures of its components at the melting point, the vapor pressure of one of the components of the melt being sufficiently high so as to substantially affect the composition of the melt because of loss by vaporization of said component, thereby ordinarily causing a change in the ratio of the components of the compound, and pulling a single crystal from the melt, said method comprising placing the compound into a melting vessel providing a vapor space about the compound, heating a part of said melting vessel closest to said compound to a temperature causing the compound to melt, heating the other parts of said melting vessel exposed to the vapor from the melt to a temperature below the melting temperature of the compound, but above the condensation temperature of the component having the highest partial vapor pressure above the melt of the compound, said space being at least sufficiently enclosed to prevent egress of component vapor, and pulling a crystal from the melt.

2. The method of melting the semiconductor compound indium arsenide (InAs) with minimized decomposition, comprising placing the compound into a melting apparatus providing a vapor space about the compound, said space being at least sufficiently enclosed to prevent egress of the vapor, heating that part of the said melting apparatus closest to the compound to a temperature causing at least a portion of the overall mass of the compound to melt, heating the other parts of the apparatus exposed to the vapor from the melt below the melting temperature of the compound but above the condensation temperature of the arsenic, the melting being in an atmosphere comprising the arsenic.

3. The method of melting with minimized decomposition a compound which exhibits substantially different partial vapor pressures of its components at the melting point, the vapor pressure of one of the components of the melt being sufficiently high so as to substantially affect the composition of the melt because of loss by vaporization of said component, thereby ordinarily causing a change in the ratio of the components of the compound, and pulling a single crystal from the melt, said method comprising placing the compound into a melting

5

vessel providing a vapor space about the compound, heating a part of said melting vessel closest to said compound to produce the molten zone therein, heating the other parts of said melting vessel exposed to the vapor from the melt to a temperature below the melting temperature of the compound, but above the condensation temperature of the component having the highest partial vapor pressure above the melt of the compound, said space being completely enclosed to prevent egress of component vapor, and pulling a crystal from the melt.

4. The method of melting the semiconductor compound indium arsenide (InAs) with minimized decomposition, comprising placing the compound into a melting apparatus providing a vapor space about the compound, said space being at least sufficiently enclosed to prevent egress of the vapor, heating that part of the said melting apparatus closest to the compound to a temperature causing at least a portion of the overall mass of the compound to melt, the melting temperature being about 936° C., heating the other parts of the apparatus exposed to the vapor from the melt below the melting temperature of the compound but above the condensation temperature of the arsenic, the condensation temperature being about 485° C., the melting being in an atmosphere comprising the arsenic.

5. In a method of zone-melting of a body of semiconductor compound in which a molten region of the compound is caused to move along the body, said compound being one which exhibits substantially different vapor pressures of its components at the melting point, the vapor pressure of one of the components of the melt being sufficiently high so as to substantially affect the composition of the melt because of the loss by vaporization of that component, thereby ordinarily causing a change in the ratio of the components of the compound, the improvement designed to substantially prevent such change, comprising zone-melting said body in a melting apparatus providing a vapor space about the compound and sufficiently enclosed to prevent egress of vapor, heating the part of the said melting apparatus closest to said compound to produce the molten zone therein, heating the other parts of the melting vessel exposed to the vapor from the melt at a temperature below the melting temperature of the compound but above the condensation temperature of the component having the highest partial vapor pressure above the melt of the compound, the melting being in an atmosphere comprising said component.

6. The method of melting and crystal pulling, with minimized decomposition, a semiconductor compound which exhibits substantially different partial vapor pressures of its components at the melting point, the vapor pressure of one of the components of the melt being sufficiently high so as to substantially affect the composition of the melt because of loss by vaporization of that component, thereby ordinarily causing a change in the ratio of the components of the compound, the melting being for the purpose of pulling a crystal from the melt, said method comprising placing the compound into a melting apparatus providing a vapor space about the compound and sufficiently enclosed to prevent egress of vapor, heating the part of said apparatus which is closest to said compound to a temperature at least sufficient to melt the compound, heating the other parts of the melting vessel exposed to vapor evolved from the molten region at a temperature below the melting temperature of the compound but above the condensation temperature of the component having the highest partial vapor pressure about the melt of the compound, and pulling a crystal from the melt, the melting being in an atmosphere comprising said component.

7. The method of claim 6, the semiconductor compound being indium arsenide.

8. In a method of zone melting the semiconductor compound indium arsenide (InAs), in which a molten region of the compound is caused to move along the body,

6

the improvement comprising zone-melting said body in an apparatus providing a vapor space about the body and sufficiently enclosed to prevent egress of vapor, heating that part of the melting apparatus closest to the said compound to produce the molten zone therein, and, as to the remaining part of the apparatus exposed to the vapor evolved from the molten region, maintaining said remaining part at a temperature below the melting temperature of the compound but above the condensation temperature of the arsenic.

9. The method of melting with minimized decomposition a compound which exhibits substantially different partial vapor pressures of its components at the melting point, the vapor pressure of one of the components of the melt being sufficiently high so as to substantially affect the composition of the melt because of loss by vaporization of said component, thereby ordinarily causing a change in the ratio of the components of the compound, and pulling a single crystal from the melt, said method comprising placing the compound into a melting vessel providing a vapor space about the compound, heating a part of said melting vessel closest to said compound to a temperature causing the compound to melt, heating the other parts of said melting vessel exposed to the vapor from the melt to a temperature below the melting temperature of the compound, but above the condensation temperature of the component having the highest partial vapor pressure above the melt of the compound, said space being at least sufficiently enclosed to prevent egress of component vapor, and pulling a crystal from the melt, the compound being a binary semiconductor compound, the components being the component elements of the compound.

10. In a method of zone-melting of a body of semiconductor compound in which a molten region of the compound is caused to move along the body, said compound being one which exhibits substantially different vapor pressures of its components at the melting point, the vapor pressure of one of the components of the melt being sufficiently high so as to substantially affect the composition of the melt because of the loss by vaporization of that component, thereby ordinarily causing a change in the ratio of the components of the compound, the improvement designed to substantially prevent such change, comprising zone-melting said body in a melting apparatus providing a vapor space about the compound and sufficiently enclosed to prevent egress of vapor, heating the part of the said melting apparatus closest to said compound to produce the molten zone therein, heating the other parts of the melting vessel exposed to the vapor from the melt at a temperature below the melting temperature of the compound but above the condensation temperature of the component having the highest partial vapor pressure above the melt of the compound, the melting being in an atmosphere comprising said component, the compound being a binary compound, the components being the component elements of the compound.

11. The method of melting and crystal pulling, with minimized decomposition, a semiconductor compound which exhibits substantially different partial vapor pressures of its components at the melting point, the vapor pressure of one of the components of the melt being sufficiently high so as to substantially affect the composition of the melt because of loss by vaporization of that component, thereby ordinarily causing a change in the ratio of the components of the compound, the melting being for the purpose of pulling a crystal from the melt, said method comprising placing the compound into a melting apparatus providing a vapor space about the compound and sufficiently enclosed to prevent egress of vapor, heating the part of said apparatus which is closest to said compound to a temperature at least sufficient to melt the compound, heating the other parts of the melting vessel exposed to vapor evolved from the molten region

at a temperature below the melting temperature of the compound but above the condensation temperature of the component having the highest partial vapor pressure about the melt of the compound, and pulling a crystal from the melt, the melting being in an atmosphere comprising said component, the compound being a binary compound, the components being the component elements of the compound.

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