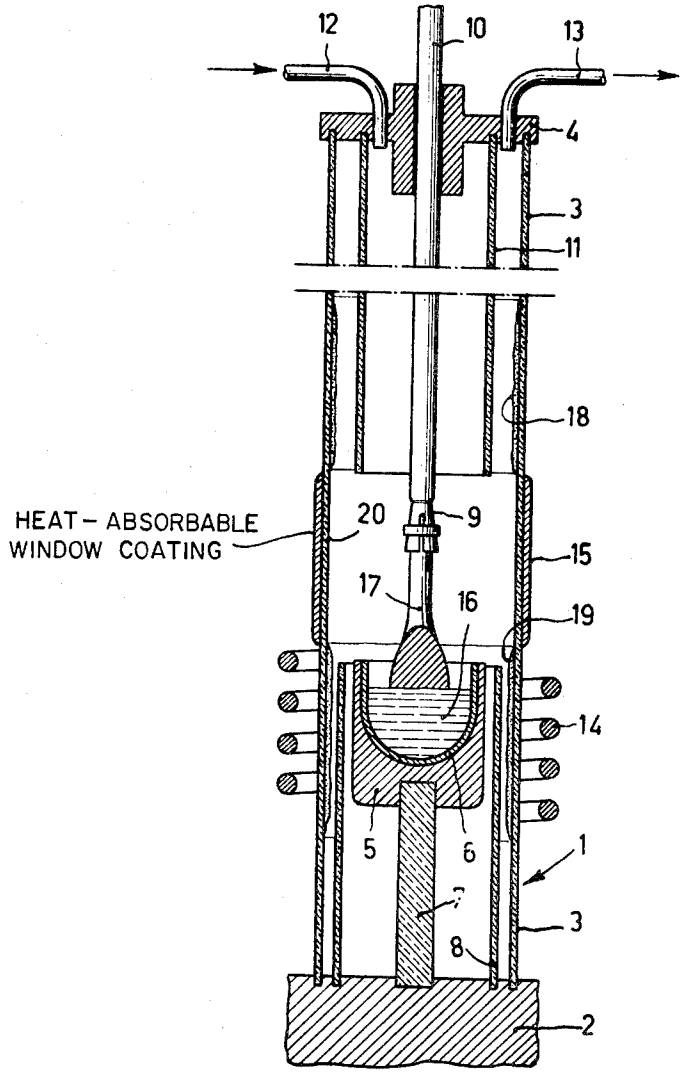
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DEVICE FOR TREATING SEMI-CONDUCTOR MATERIALS BY MELTING

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# DEVICE FOR TREATING SEMI-CONDUCTOR MATERIALS BY MELTING

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The invention relates to devices or apparatus for treating fusible semi-conductor materials by melting in a chamber, the walls of which are at least partly transparent. Such a chamber may be employed for example for protecting the material to be treated from atmospheric influences and/or for adjusting the desired gas atmosphere or a vacuum during the treatment. Such devices are used, for example, to obtain crystals of such a semiconductor material by pulling them up from a melt or to subject such a material to zone-melting processes, for example for purifying it, to dope it or to change it over to the mono-crystal form. In such treatments it is desirable to be in a position to observe the course of the process, in order to be able to control the process and adjust it, if required. For example with the crystal-pulling method the variation of the diameter of the growing crystal can be observed and in accordance with the observation the diameter may be brought to the desired value by adjusting the temperature of the melt or of the rate of pulling. With zone-melting the length of the molten zone may be observed and be adjusted by means of the supply of energy to the molten zone. With floating zone-melting, in which a molten zone traverses a rod-shaped body of the material to be treated and the two ends of the rod-shaped body are fastened to a holder, the diameter of the growing rod can be observed and adjusted by varying the distance between the holders. All these modes of control and adjustment on the basis of direct observation of the phenomena inside the chamber are known per se.

The wall of the chamber consists in this case, at least in part of a transparent material, for example quartz glass.

It had been found that difficulties may arise owing to the formation of a deposit on the inner wall of the treating chamber during the process. Such a deposit was found to hinder a normal view of the process in many cases.

There have been proposed several steps to ensure an observation during the treatment.

It has been proposed for example to provide the chamber with a comparatively narrow, cooled side tube having a window at the end. The side tube may be sealed to a cylindrical quartz-glass wall of the chamber. Such a cylindrical part with a side tube is fairly complicated and a normal replacement of the quartz cylinder after repeated use is fairly costly. Moreover, the field of view is much restricted.

In accordance with a further known proposition (see British Patent 826,575) there is provided a screen wiper inside the chamber, so that a transparent part of the chamber wall can be cleaned. The actuation of the screen wiper from the outer side renders the device complicated an such an additional part inside the chamber raises the risk of contamination of the semi-conductor material.

The invention has for its object to provide inter alia a simple measure to prevent the formation of a deposit on at least one wall portion or to reduce it to an extent such that observation of the phenomena inside the chamber remains possible. It is based on the one hand on



the idea to prevent the local formation of a deposit on a wall portion by heating this portion at a higher temperature than an adjacent wall portion and on the other hand it is based on the idea to utilise the heat radiation from the heated parts inside the chamber for heating a transparent wall portion. With devices of the kind set forth transparent wall portions of quartz glass are used so far. Quartz glass has a low absorption power for heat and infrared radiation, so that the known quartz glass wall is heated only to a small extent by the infrared radiation and/or heat from the molten material inside the chamber.

In accordance with the invention, at least one transparent wall portion is used which has a higher absorption power for heat radiation than the adjacent wall portions. Such a transparent wall portion may, in principle, consist entirely of a transparent material having a comparatively high absorption power for heat radiation. For the adjacent portions use may be made of a conventional material having a poor absorption power for such a radiation, for example quartz glass.

It should be noted that a device for floating zone-melting of gallium-arsenide has been proposed, in which a chamber with a vertical, tubular quartz glass wall is arranged so as to be vertically movable inside two superimposed resistor furnaces, spaced apart from each other, and in the interval between the furnaces a high-frequency coil is arranged for the formation of the molten zone. Between the furnaces the molten zone can be observed through the quartz glass wall. In order to prevent the quartz glass wall portion between the furnaces from forming the colder part of the device it has been proposed to dispose between the two furnaces an annular, transparent quartz body provided with a platinum heating wire between the coil and the chamber wall in order to heat the latter locally. Such a wired ring is fairly complicated, the more so as the wiring must be such that it withdraws a minimum of high-frequency energy from the field of the coil.

In accordance with the invention, at least on one portion of a transparent chamber wall there is preferably provided a layer of a transparent material having a higher absorption power for heat and/or infrared radiation than the material of the substratum. This layer is preferably applied to the outer side of the chamber. In the latter case any risk of contamination of the semi-conductor material need not be taken into consideration in choosing the composition of the layer.

The transparent material of the layer consists preferably at least mainly of tin oxide, indium oxide or mixtures thereof. It may contain, if desired, also other constituents, for example, antimony, phosphorus, boron, fluorine, copper, cadmium, vanadium, chromium, manganese and/or cobalt. A further suitable material is for example cadmium oxide, if desired with additions such as indium oxide. Transparent materials of this kind are known per se and may be applied in thin layers for example of a thickness of 0.1$\mu$ to a transparent substratum, for example of glass. To this end a solution of compounds of the metals to be used in such a layer, for example halides of these metals in a suitable solvent, for example alcohol or concentrated hydrochloric acid, may be sprayed in the form of fine drops on a preheated substratum. The substratum consists preferably of quartz glass. A portion of the transparent wall is preferably coated with the layer and the coated portion is completely surrounded by non-coated portions of the same material as the substratum of the layer. The layer may be electrically conductive. This is for example the case with layers consisting at least mainly of tin oxide and/or indium oxide. An additional heating may be pro-

vided by passing an electric current through the layer with the aid of electrodes secured to the layer, for example, if it is found that the effect of the heat and/or infrared radiation produced inside the chamber is insufficient to avoid hindrance of view in the long run, though this is normally not required.

If such a conductive layer is used on an annular, transparent wall portion inside a high-frequency coil provided for heating the molten material, the layer extends preferably over part of the circumference of the annular portion only. The layer may for instance be divided into one or more non-joined portions. Thus it is avoided that the conductive layer absorbs an excessive quantity of high-frequency energy, which might prevent an effective heating of the zone inside the chamber.

The layer is preferably provided on an annular, transparent wall portion outside the high-frequency coil and coaxially to this coil, the layer forming a closed ring. Thus the layer is capable of absorbing part of the energy of the high-frequency field of the coil and be thus additionally heated, however, without hindering an effective heating of the material to be treated inside the chamber.

The invention will be described more fully with reference to the accompanying drawing, in which the figure shows diagrammatically a front elevation of a device for pulling crystals from a melt in a vertical sectional view.

The device shown in the figure comprises a chamber **1** formed by a bottom **2**, a vertical, cylindrical quartz glass tubular wall **3** having a wall thickness of about 2.5 mms. and a lid **4**. Inside the chamber there is arranged a crucible comprising an outer crucible **5** of graphite and an inner crucible **6** of quartz. The crucible is supported from a quartz glass support **7**, which bears on the bottom **2** of the chamber **1**. The crucible is surrounded by a cylindrical radiation screen **8** of sintered quartz, which also bears on the bottom **2** of the chamber. A holder **9** for a crystal to be pulled up is fastened to a vertical rod **10**, which is taken through the lid **4** in a gas-tight manner, so as to be movable and which can be moved vertically and rotated about its axis by a mechanism (not shown). The gas-tight passage of the rod **10** through the lid **4** is not shown in detail in the figure, nor is the mechanism for moving the rod **10** vertically with a controllable speed and to cause the rod to rotate, but these may be realised in known manner, not essential for the present invention. Inside the chamber **1** the rod **10** is surrounded coaxially by a quartz-glass tube **11**, which is fastened to the lid **4**. Through the lid are taken a gas inlet **12**, opening out in the tube **11**, and a gas outlet **13** opening out inside the chamber and outside the tube **11**, so that a gas of the desired composition can be passed through the chamber. At the level of the crucible the chamber is surrounded by a high-frequency coil **14**, which is connected to a high-frequency generator (not shown).

On the outer side of the cylindrical tube wall **3** there is provided, on a portion above the crucible, an annular layer **15** of transparent tin oxide of a thickness of about 0.3$\mu$. The portion of the tube wall **3** coated with this layer is located so that via this wall portion a satisfactory view of the interior of the crucible can be obtained.

The layer **15** was provided in the following way.

The outer surface of the quartz-glass tube **3** having, for example, an outer diameter of 12.5 cms. should be covered over its wall portion **20** having a length of, for example, 10 cms. with the tin oxide layer **15**.

To this end the outer surface of the tube **3** with the exception of the wall portion **20**, is covered with a slurry consisting of an aqueous dispersion of graphite powder, comprising also a suitable binding agent and sold under the trademark name "Aquadac." The tube **3** is placed coaxially inside a cylindrical resistance furnace, having a length of 6 cms. and an inner diameter of 20 cms. such that the wall portion **20** is in the middle of the furnace. The furnace is heated such that the temperature of the wall portion **20** is about 600° C.



A spraying solution is prepared by mixing 300 mls. waterfree tintetrachloride, 3000 mls. butylacetate, and 5 mls. concentrated hydrofluoric acid (40% by weight). By means of a spray-gun, the nozzle of which is placed at one of the openings of the furnace between the inner furnace wall and the outer tube wall, in total 60 mls. of the above spraying solution is sprayed between the said two walls. The total amount of 60 mls. is not sprayed continuously, but each time about 15 mls. is sprayed during about one minute using intervals of about 10 minutes before spraying the next portion of 15 mls. During spraying the spray gun is moved such that its nozzle makes a circular movement concentrically around the tube. During each interval the gun is placed with its nozzle at the opposite opening of the furnace in a similar way as described before.

Due to evaporation of the solvent of the liquid, sprayed in this way onto the outer surface of wall portion **20**, the temperature of this wall portion is lowered. For obtaining a good, transparent tin oxide coating the temperature of the wall portion **20** should not drop to temperatures below 450° C. during spraying. Therefore the total amount of 60 mls. of the spraying solution is not sprayed continuously, but after spraying 15 mls. at a time the wall portion **20** is allowed to regain the temperature of 600° C. before spraying the next 15 mls. After having sprayed the last amount of 15 mls. heating is continued for another 10 minutes after which the furnace is extinguished and furnace and tube are allowed to cool down to room temperature. The tube **3** is removed from the surface and the tin oxide at these wall portions having been covered with the carbon slurry, is removed simply by rubbing. The tin oxide layer on the outer surface of the wall portion **20** sticks rather firmly to the quartz-glass wall and has a thickness of about 0.3$\mu$. The tin oxide of the layer further comprises minor amounts of fluorine.

The process of applying the tin oxide layer **15** is given above by way of example. It could be varied easily by those skilled in the art and other processes may be used also, such processes, as such, being not essential for the present invention.

Hereinafter the use of the device described with reference to the drawing for producing silicon monocrystals will be explained. The inner crucible **6** contains to this end a silicon charge and the crystal holder **9** has fastened to it a silicon seed crystal.

Via the gas inlet **12** and the gas outlet **13** a flow of an inert gas is passed through the chamber **1**, for example argon of approximately atmospheric pressure. The high-frequency coil **14** is then energized by means of the high-frequency generator, so that inductance currents produce heat in the outer crucible **5**. The silicon charge is thus heated, so that a silicon melt **16** is formed in the crucible. The rod **10** is then moved downwardly until the seed crystal touches the melt with its lower end, after which the rod **10** is moved upwardly with a speed of for example approximately 1 mm. per minute, while it is rotated about its axis at the rate of about 60 r.p.m. During the upward movement of the rod **10** the seed crystal fastened to the holder **9** grows, so that a monocrystal **17** of silicon is formed. In known manner the thickness of the growing crystal can be controlled by controlling the current intensity in the high-frequency coil and/or by controlling the pulling rate.

The molten silicon is found to react with the quartz of the inner crucible **6**, so that silicon monoxide is formed, which escapes in the form of a vapour and may settle on the colder portions of the chamber walls, so that a more or less brown deposit **18** and **19** is produced on the quartz glass wall of the chamber, which reduces the transparency of this wall. The tin oxide layer **15** absorbs heat radiation from the crucible and the melt and locally heats, by heat conduction, the wall portion **20** coated with the layer **15**. Since otherwise the quartz glass of the wall **3**

does not absorb heat from the crucible and the melt, substantially the temperature of the wall portions adjacent the wall portion **20** remains much lower than that of the wall portion **20**. The wall portion **20** may assume a temperature of about 500° C. to 600° C., while the adjacent wall portions are heated at a lower temperature of for example between 200° C. and 300° C. It is found that no deposit is formed on the wall portion **20**, which may be ascribed to the high temperature difference between the wall portion **20** and the adjacent wall portions. The colder wall portions might keep the vapour pressure of the silicon monoxide so low that a deposition on the hotter wall portion **20** could no longer take place.

The wall thickness of the absorptive layer **15** is chosen to attain a wall temperature at which substantially no deposit is formed, while retaining its optical transparency to permit observation of the chamber interior. Thus, for example, a thicker layer **15** will cause the substrate wall to assume a higher temperature than if the layer were thinner. The thickness to be employed will also depend upon the amount of vapor being formed and deposited on the wall limiting external observation of the chamber interior. Those skilled in the art will have no difficulty in determining a suitable layer thickness based upon the foregoing teachings, e.g. within a range from $0.1\mu$ up to $0.7\mu$.

It has furthermore been found that, if the tin oxide layer **15** is not applied to the wall portion **20**, also this portion gets a brownish deposit of silicon monoxide. It should be noted here that in the present case the layer **15** is at the same time electrically conductive and may additionally be heated by the absorption of high-frequency energy of the coil. However, it has been found that with the use of the layer **15** in the form of an open ring no deposit of silicon monoxide is formed, in general, on the portion of the quartz glass wall covered by the layer.

It should be noted that the present invention is not restricted to the use of tin oxide and that for example also transparent layers of other materials may be used, for example on the basis of indium oxide. The invention is furthermore not restricted to pulling silicon crystals from a melt, but it may also be carried out with thermal treatments of other materials, in which case other condensation products than silicon monoxide may be deposited, for example the material itself or decomposition products thereof. Moreover, the layer may be provided with electrodes and an electric current may be passed through the layer in order to attain a higher wall temperature than can be obtained by means of absorbed heat radiation alone. Finally, the invention is not restricted to devices for pulling up crystals from a melt; it may also apply to other devices of melting semi-conductor materials, for example devices for zone melting, for instance floating zone melting. The invention may also be applied to devices for applying semi-conductor material by vaporization to a support, in which the semi-conductor material is evaporated from a melt of this material in an exhausted chamber.

What is claimed is:

**1.** Apparatus for treating semiconductive materials by melting which semiconductive materials when molten produce vapors capable of forming opaque deposits, comprising a chamber having wall portions and within the chamber means for supporting a crystalline rod-like body of said semiconductive material with respect to a melt, means for heating at least a portion of the semiconductive material at a temperature at which it melts, a wall portion of said chamber being at least partly transparent and serving as an observation window for the melt, said observation window being exposed to the melt and thus subject to the growth of said opaque deposits thereon which obscure continued observation of the melt through



the window, and integral with said observation window a material having a higher absorption power for heat radiation than materials of adjacent wall portions of the chamber whereby the said observation window is maintained by absorption of heat radiation at a higher temperature than the adjacent wall portion thereby reducing the tendency for deposits to grow thereon and obscure vision therethrough.

**2.** Apparatus as set forth in claim **1** wherein the supporting means comprises a crucible for the melt, and there is also included means for pulling a crystal of semiconductive material from a melt in said crucible, said observation window being located above the crucible.

**3.** Apparatus for treating semiconductive materials by melting which semiconductive materials when molten produce vapors capable of forming opaque deposits, comprising an enclosure having wall portions and within the enclosure means for supporting a crystalline rod-like body of said semiconductive material with respect to a melt, means for heating at least a portion of the semiconductive material at a temperature at which it melts, a wall portion of said enclosure being of a substantially transparent material and serving as an observation window for the melt, said observation window being exposed to the melt and thus subject to the growth of said opaque deposits thereon which obscure continued observation of the melt through the window, and on the outside of said observation window a layer of a substantially transparent material having a higher absorption power for heat radiation than the material of the enclosure wall portions whereby the said observation window is maintained by absorption of heat radiation from the melt at a higher temperature than the adjacent wall portions thereby reducing the tendency for deposits to grow thereon and obscure vision therethrough.

**4.** Apparatus as set forth in claim **3** wherein the layer consists essentially of at least one substance selected from the group consisting of tin oxide and indium oxide.

**5.** Apparatus as set forth in claim **3** wherein the layer is a metal oxide having a thickness between about 0.1 and 0.7 micron and the enclosure wall portions are of quartz.

**6.** Apparatus as set forth in claim **3** wherein the heating means includes a high-frequency coil surrounding the enclosure, and the layer is electrically conductive and is applied to an annular portion of the observation window, said layer being interrupted and covering only part of the circumference of the annular portion.

**7.** Apparatus as set forth in claim **3** wherein the heating means includes a high-frequency coil surrounding the enclosure, and the layer is electrically conductive and is applied to an annular portion of the observation window which is spaced from and lies above the high-frequency coil, said layer forming a closed ring.

**8.** Apparatus as set forth in claim **3** wherein the enclosure is of transparent quartz, and the observation window is formed by the enclosure wall portion covered by the higher absorbing layer.


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