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METHOD OF MANUFACTURING SEMI-CONDUCTIVE BODIES HAVING ADJOINING ZONES OF DIFFERENT CONDUCTIVITY PROPERTIES

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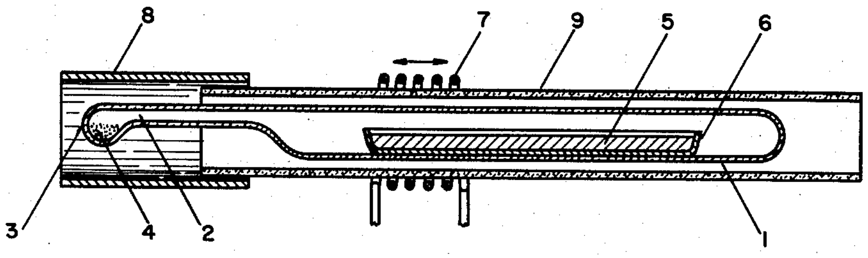

Fig. 1

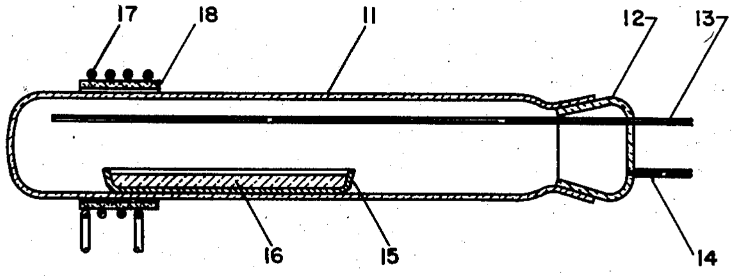

Fig. 2

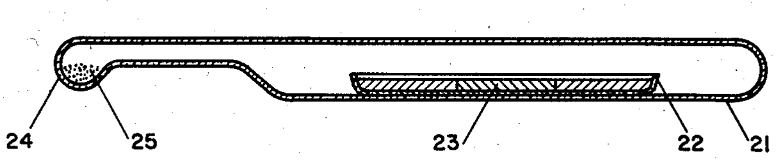

Fig. 3

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METHOD OF MANUFACTURING SEMI-CONDUCTIVE BODIES HAVING ADJOINING ZONES OF DIFFERENT CONDUCTIVITY PROPERTIES

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This invention relates to the manufacture of semi-conductive bodies having adjoining zones of different conductivity properties, more particularly of opposite types of conductivity, which may be used in asymmetrically conductive devices such as rectifiers, transistors, photo-electric cells and phototransistors.

It is known to obtain such semi-conductive bodies by segregating semi-conductive material from a melt, if after segregation of part of the material having a determined conductivity, a substance is added to the melt to permit segregation of further material of different conductivity properties, more particularly of opposite conductivity type. The added substance may be an acceptor or donor impurity, an impurity decreasing the concentration of electrons or holes, or an impurity acting upon the life-time of minority charge carriers.

Thus, germanium which exhibits n-conductivity due to a content of arsenic may have a small amount of gallium added to it during segregation, whereupon p-type germanium deposits. If desired, a body having a plurality of zones of different conductivity properties may be obtained by adding alternately donor and acceptor impurities during segregation.

Furthermore, it is known that this result may be obtained by utilizing a semi-conductive body of determined conductivity and alloying it locally with a substance which locally results in semi-conductive material of different conductivity properties, more particularly of opposite conductivity type. For example, a body of germanium which is fully n-conductive due to a content of antimony may be locally alloyed with indium so as to become in part p-conductive.

The known methods may be used for obtaining semi-conductive bodies, for example, consisting of germanium, silicon and also of compounds such as InSb, PbS and the like. The doping in the solid state with foreign atoms and in the case of compounds also of constituents of the lattice of the compounds, which are decisive for the conductivity properties, is no simple task with the small concentrations entering into consideration therefor.

According to the invention, the said disadvantage is obviated in that in the manufacture of semi-conductive bodies having adjoining zones of different conductivity properties, more particularly of opposite conductivity type by segregation from a melt, the concentrations of foreign atoms and/or constituents of the lattice are controlled by doping in the melt via the vapour phase.

It will be evident that in the invention, for acting upon the conductivity properties, use is made only of substances which can be present in vapour in a noticeable concentration at the temperature at which the semi-conductive material is maintained in a molten state in carrying out the method.

Dosing small amounts of material in the melt via the vapour phase does not involve any particular difficulties.

The amount taken up by the melt from the atmosphere or given off thereto may be influenced by means of the temperature of the melt and the vapour pressure of the substance prevailing above the melt. The temperature of the melt may readily be controlled accurately whereas the vapour pressure may be controlled in different ways, as will be explained more fully hereinafter.

In the method according to the invention, use may be made, for example, of material which as a result of its purity does not sufficiently exhibit the conductivity properties desired in one of the parts of the semi-conductive body to be manufactured. In this case the semi-conductive material is fused and brought into interaction with a vapour. After the melt has taken up so many foreign atoms and/or constituents of the compound from the vapour that, taking into consideration the distribution coefficient (defined as the ratio between the concentrations in the segregated material and in the melt), the desired conductivity properties after segregation may be expected, part of the material is segregated. Subsequently, another vapour which may cause different conductivity properties is brought above the material which is still in the molten state. After the required concentration of foreign atoms and/or constituents of the compound is attained, the material is allowed to segregate further, so as to obtain a semi-conductive body having two adjoining zones of different conductivity properties, more particularly of opposite conductivity types. The treatment may be repeated if more zones of different conductivity properties are desired in the semi-conductive body.

According to the invention, it is alternatively possible to start from semi-conductive material which already contains substances, due to which after segregation from a melt it exhibits a conductivity as is desired for part of the body to be formed. In this case part of the material is caused to segregate from the melt. If the material contains volatile foreign atoms and/or volatile constituents, evaporation thereof may be counteracted by means of vapour above the melt. Subsequently, the melt is brought into interaction with vapour of an impurity and/or a volatile constituent which can cause a different conductivity or a conductivity of opposite type, the material being allowed to segregate further so as to obtain a body having zones of different conductivity properties. If more such zones are desired in juxtaposition, this may be achieved by varying periodically the vapour pressure of the said volatile constituent above the melt during segregation.

Instead of taking up substances from the vapour phase by a melt, it is alternatively possible to give part of the body the desired variation in conductivity by evaporating a volatile impurity and/or constituent. It is then possible, for example, to utilize semi-conductive material containing several impurities which can cause conductivity of opposite type and of which one is predominant in concentration, at least the last-mentioned impurity and/or at least one of the constituents in a semi-conductive compound being a volatile substance. In this case part of the material is allowed to segregate, the melt being brought into interaction with an atmosphere in which the vapour pressure of the volatile substance or substances is so high that evaporation from the melt is counteracted. Subsequently, the melt is brought into interaction with an atmosphere in which the vapour pressure of the substance or substances is so low that evaporation from the melt takes place, with the result that upon further segregation material of different conductivity, more particularly of opposite conductivity type deposits. More zones of different conductivities may be obtained by alternately increasing and decreasing the vapour pressure of the volatile substance or substances during segregation.

In the foregoing, reference was always made to segregation of the semi-conductive material from a melt. This may be effected in different ways. It is possible, for example, to fuse the whole mass and to allow cooling of the melt from one side of the charge, or to draw up a crystal from the melt. As an alternative, the material may be locally melted and allowed to segregate or zone melting may be used, in which event a molten zone is caused to traverse a charge of the semi-conductive material and segregation is effected at one of the zone boundaries.

The vapour pressure of the impurities and/or constituents of a semi-conductive compound may be controlled in different ways. When use is made of an open melting vessel, the vapour pressure may be controlled by means of a flow of gas charged with vapour from the said substances or with a compound producing the said vapour.

If the melting process is carried out in a closed vessel, the vapour pressure of the said substances may be controlled by means of the temperature given to an amount of such a substance or a compound which upon heating produces a corresponding vapour, which substance or compound is introduced into the vessel separately from the charge of semi-conductive material to be treated. The substance or compound must in this case be heated to a temperature providing the desired vapour pressure at the most equal to, but preferably lower than that of the other parts of the vessel. The vessel may either be exhausted, or an inert filling of gas may be used to avoid evaporation of the semi-conductive material during melting.

In carrying out the method, there is interaction between the molten semi-conductive material and the atmosphere prevailing above the melt.

Since crystals split off from the melt having a composition which differs from that of the melt, the composition of the melt is continuously varied during segregation. It is possible that the variation in the composition of the melt as a result of segregation takes place more slowly than the adjustment of the equilibrium between the melt and the atmosphere. Consequently, there is always a condition of equilibrium and the conductivity properties may be exactly controlled and varied by means of the pressure of the vapour. However, the conditions may also be such that the variation in the composition of the melt as a result of segregation takes place more slowly than the adjustment of the equilibrium between the melt and the atmosphere, so that it is difficult to obtain this equilibrium. However, in such cases it is nevertheless possible to achieve a stationary condition and thus a reasonable reproducible action upon the composition of the melt and of the conductivity properties of semi-conductive bodies obtained therefrom by segregation. It is dependent upon the duration of the interaction between the melt and the atmosphere as to whether equilibrium or a stationary condition is obtained. It is therefore desirable to maintain the semi-conductive material in the molten state for a long period, to provide a large surface area of the melt and to carry out the segregation process at a slow rate.

An advantageous circumstance in the method is furthermore that the melt may take up vapour from, or give off vapour to the atmosphere at a considerably quicker rate than does the semi-conductive material in the solid state. Consequently, in so far as interaction between the atmosphere and segregated material takes place, the interaction will be limited to the surface. If necessary, this surface may be removed, for example by etching. Otherwise, the said interaction may be counteracted to a considerable extent by maintaining the segregated solid substance at a low temperature.

Example I

For manufacturing semi-conductive bodies having p-n junctions from PbS by zone melting, use may be made, for example, of an apparatus as shown diagrammatically in Fig. 1 of the accompanying drawing.

Reference numeral **1** indicates a tubular container exhibiting a contraction **2**, resulting in a space **3** in which a substance **4** which can supply vapour upon increase in temperature is provided separately from the charge of the compound **5** to be treated, which is contained in a vessel **6** of sintered aluminium oxide. The local heating for melting a zone of the charge of the compound **5** is effected with the use of a high-frequency coil **7**. For heating the substance **4** use may be made of an electric oven **8** and for heating the remaining part of the vessel **1** use may be made of a coal oven **9**.

The vessel **6** is filled with 50 gs. of pure PbS (impulrties less than 10^{-2} atm. percent) and the space **3** is filled with sulphur, the container **1** subsequently being exhausted. The part of the container containing the vessel **6** is heated to 500° C. The sulphur is heated to a temperature of 444° C. and produces a sulphur pressure of 1 atm. in the whole of the container. The temperature is locally increased to 1150° C. by means of coil **7**, which is moved from the left to the right at a speed of 1 mm. per minute. The PbS segregating at the edge of the melting zone exhibits p-conductivity by including sulphur in the lattice to a concentration higher than that corresponding to the composition PbS. That is, under these conditions, excess sulphur is taken up by the melt.

After the molten zone has traversed about half of the charge, the coil is stopped and the oven **8** is cooled down to a temperature of 400° C., the vapour pressure of the sulphur thus being decreased to 0.4 atm. Subsequently, the coil is set into movement again. PbS of n-type conductivity now segregates at the edge of the melting zone due to the sulphur pressure of 0.4 atm. being in equilibrium with a melt containing a smaller amount of sulphur than corresponds to the composition PbS. That is, under these conditions, the melt gives off sulphur resulting in a deficiency thereof. After cooling, the rod is removed from the apparatus.

The p-type PbS which first segregated has a specific resistance of 3×10^{-2} ohm cm. and the PbS of n-type conductivity which subsequently segregated has a specific resistance of 4×10^{-3} ohm cm. The p-n junction is very sharp and has rectifying properties.

Example II

Use is made of an apparatus as shown diagrammatically in Fig. 2, reference numeral **11** indicating a quartz container closed by a ground joint **12** exhibiting an inlet tube **13** and an outlet tube **14** for the gas flow intended to act upon the conductivity properties of the substance to be treated.

The quartz container **11** contains a vessel **15** of sintered aluminium oxide filled with lead sulphide **16**. For the local melting of a zone of the substance to be treated, use is made of a high-frequency coil **17** which comprises an inner graphite ring **18** for the thermal transmission.

Lead sulphide is melted and segregated in a gas flow consisting of a mixture of H_2 and H_2S, by which a given sulphur pressure is adjusted dependent on the temperature. Since at the melting point of PbS (1114° C.) H_2S provides a sulphur pressure of 0.1 atm., pure molten PbS in H_2S would always provide n-type material. In view thereof use was made of PbS containing 0.5% of Ag, viz. 125 mgs. of Ag_2S for 50 gs. of PbS, which upon being melted and segregated in an H_2S flow provides p-type material and in a mixture of H_2 and H_2S provides n-type material. The zone in the charge of silver-containing lead sulphide, which zone is melted by means of coil **17**, is exposed alternately to an H_2S flow and to a flow consisting of a mixture H_2S; H_2=2:1. The coil **17** is moved from the left to the right at a speed of 2 mms. per minute. Each time the gas atmosphere is changed, which thus changes the sulphur vapor pressure, the coil is stopped until the atmosphere has sufficiently adapted itself. Three p-n junctions are thus produced in the charge. The p-n junctions are very sharp and the specific resistance in the parts having p-type and n-type conductivity is about 6×10^{-4} ohm. cm.

Example III

PbS containing 0.5% of Ag is treated in a device as shown in Fig. 2. A zone in the lead sulphide is melted by means of coil **17**, this zone being moved through the charge from the left to the right at a rate of 2 mms. per minute. At first a gas-mixture $H_2S:H_2$ is 75:5 and subsequently a mixture of the composition

$$H_2S:H_2:HCl=75:5:1$$

is lead through. When the composition of the gas flow is changed, the coil is stopped until the atmosphere in the vessel has adapted itself. The part segregated in the gas flow of the first-mentioned composition exhibits p-type conductivity and a specific resistance of 1.2×10^{-2} ohm. cm. The part deposited in the HCl-containing atmosphere is n-conducting and has a specific resistance of about 6×10^{-4} ohm. cm.

Example IV

An amount of InSb is treated in a device as shown diagrammatically in Fig. 1. The vessel **6** of sintered aluminium oxide is filled with InSb and the space **3** is filled with an amount of mercury. After being exhausted, the vessel except the space **3** is heated to a temperature of 400° C. A zone is melted at 530° C. by means of the high-frequency coil which is moved from the left to the right at a speed of 2 mms. per minute as far as approximately the centre of the charge. Subsequently, the space **3** is heated to 357° C. by means of the oven **8**, resulting in an Hg-vapour pressure of 1 atm. above the melt. Subsequently, the molten zone is caused to move further through the charge. The part segregated in vacuo exhibits n-conductivity, the number of charge carriers being 1.4×10^7 per cm.^{3} and the specific resistance being 2.9×10^{-3} ohm. cm. The part segregated under mercury vapour exhibits p-conductivity, the number of charge carriers being 1.45×10^{18} per cm.^{3} and the specific resistance being 6.7×10^{-3} ohm cm.

Example V

CdTe is treated in a device as shown in Fig. 1. The CdTe is contained in a vessel **6** of graphite and the space **3** is filled with an amount of Cd. Indium is added to the left-hand side of the charge to an amount such that, when a zone of 2 cm. wide is provided by melting, an in-concentration of 10^{19} atoms per cm.^{3} is obtained. After being exhausted, the vessel is heated to 900° C. with the use of the oven **9**. The space **3** is heated to 750° C. by means of the oven **8**, as a result of which a Cd-pressure of 1 atm. prevails in the whole vessel. Subsequently, a zone of the charge is melted at 1040° C. by means of the coil **7**, which is moved from the left to the right at a rate of 5 mms. per minute. After approximately half of the charge has been traversed by the molten zone, the temperature of the Cd in the space **3** is decreased to 650° C., resulting in a decrease of the Cd-pressure to 0.3 atm. Subsequently, the residue of the charge is traversed by the molten zone.

The in-containing CdTe which has segregated at 1 atm. Cd is n-conductive, the number of charge carriers being 2.8×10^{17} per cm.^{3} and the specific resistance being 0.04 ohm cm. The part of the charge segregated at 0.3 atm. Cd is p-conductive, the number of charge carriers being 5×10^{16} per cm.^{3} and the specific resistance being 1.5 ohm cm.

Example VI

The central portion **23** of a monocrystal rod of p-conductive germanium contained in a suitable quartz vessel **22**, as shown in Fig. 3, is melted at 965° C., for example by high-frequency heating, in a vacuum container **21**. The part **24** of the quartz vessel contains an amount of As 25. The As is heated to 400° C. and provides an As-pressure of 6 mms. mercury in the vessel **21**, which is heated to 500° C. After 20 minutes, by slowly decreasing the temperature, the crystal is allowed to grow again to the centre at a speed of about 1 mm. per minute. After this treatment, during which As atoms have been absorbed, the central portion **23** of the p-germanium having a specific resistance of 1.5 ohm cm. is converted into n-germanium having a specific resistance of 0.05 ohm cm. Very sharp p-n junctions are produced at the two limits of the zone which has been melted. The surface of the parts of the germanium crystal which have not been melted is covered during treatment with an n-conductive film, which may be removed by etching.

What is claimed is:

1. A method of producing a semi-conductive body containing a p-n junction, which comprises providing a semi-conductive body containing a volatile constituent which tends to evaporate out of the semi-conductive body when the latter is in a molten state, melting and freezing adjacent portions of said semi-conductive body in the presence of a vapor of said volatile constituent, and establishing a p-n junction in said body by varying the vapor pressure of said volatile constituent between two extremes while melting and freezing said adjacent portions of said semi-conductive body whereby at one extreme of said pressure one of said molten portions of the body takes up said volatile constituent and upon subsequent freezing produces one type of conductivity material, and at the other extreme of said pressure the adjacent molten portion gives off said volatile constituent and upon subsequent freezing produces the opposite type of conductivity material, said frozen adjacent portions establishing a p-n junction within the body.

2. A method of producing a semi-conductive body containing a p-n junction, which comprises providing a semi-conductive body constituted of a chemical compound containing a volatile constituent and whose conductivity type depends on an excess or deficiency of said volatile constituent in said body when frozen, melting and subsequently freezing one portion of said body in the presence of a vapor of said volatile constituent at a pressure at which the molten portion takes up an excess of said volatile constituent to produce one conductivity-type material upon freezing, and establishing a p-n junction within the body by melting and subsequently freezing another portion of said body in the presence of said vapor of said volatile constituent but at a lower pressure at which said other molten portion gives off said volatile constituent yielding a deficiency therein and the opposite conductivity-type material upon freezing, said frozen portions establishing a p-n junction within the body.

3. A method as set forth in claim 2, wherein the melting and freezing steps are carried out by a zone-melting process.

4. A method as set forth in claim 2, wherein the melting and freezing steps are carried out by first melting the body and drawing up a crystal from the melt to freeze successive portions thereof.

5. A method as set forth in claim 2 wherein the melting and freezing steps are carried out in an open vessel, and the vapor of the volatile constituent is provided by flowing a gas containing said volatile constituent through said vessel.

6. A method of producing a semi-conductive body containing a p-n junction, which comprises providing a closed vessel having first and second portions, providing in said first vessel portion a semi-conductive body constituted of a chemical compound containing a volatile constituent and

whose conductivity type depends on an excess or deficiency of said volatile constituent in said body when frozen, providing in said second vessel portion a material which produces said volatile constituent upon being heated, heating said material in said second vessel portion at a temperature producing in said first vessel portion a vapor of said volatile constituent, heating said semi-conductive body in said first vessel portion at a higher temperature to melt a portion of said body and subsequently freezing said one body portion in the presence of the vapor of said volatile constituent at a pressure at which the molten portion takes up an excess of said volatile constituent to produce one conductivity-type material upon freezing, and establishing a p-n junction within the body by melting and subsequently freezing another portion of said semi-conductive body in the presence of said vapor of said volatile constituent but at a lower pressure at which said other molten portion gives off said volatile constituent yielding a deficiency therein and the opposite conductivity-type material upon freezing, said frozen portions establishing a p-n junction within the body.

7. A method as set forth in claim 6 wherein the vessel is first exhausted before the heating steps.

8. A method as set forth in claim 6 wherein the vessel contains an inert gas.

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