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Mead et al.

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[54] **METHOD FOR PROCESSING SEMICONDUCTORS**

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[52] **U.S. Cl.** ....**117/201,** 117/201, 117/114 A, 117/120, 148/1.5, 148/20.6

[51] **Int. Cl.** **C23c 13/04,** C23c 17/00, H011 7/46

[58] **Field of Search** ....148/1.5, 186, 20.6; 117/201, 117/227, 114 A, 113, 120, 102 R

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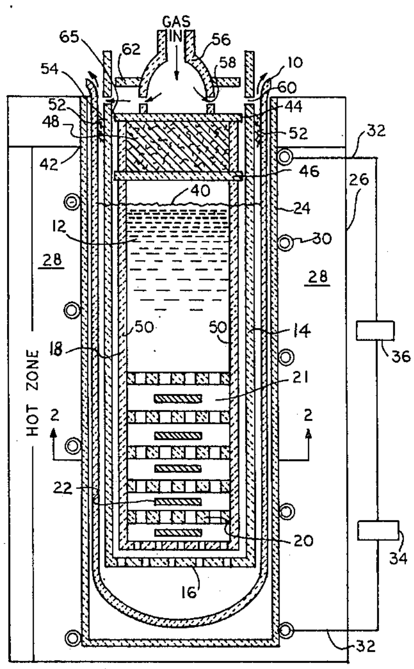
[57] **ABSTRACT**

A system for diffusion treatment of semiconductor compounds including an open crucible containing a molten bath of treating material and a liquid permeable carrier member for inserting and removing semiconductor slabs from the bath. The bath is isolated from reacting with the atmosphere by slowly flowing an inert gas across the top of the bath. High melting point treating materials such as zinc can be more readily removed from semiconductors such as zinc sulfide by quickly removing the carrier from the zinc bath and inserting the carrier into a bath of a material having a much lower melting point such as indium or gallium. The lower melting material displaces the higher melting material and the lower melting material is then mechanically removed from the slabs while being heated on a hotplate to a temperature above the melting point of the lower melting material.

15 Claims, 4 Drawing Figures



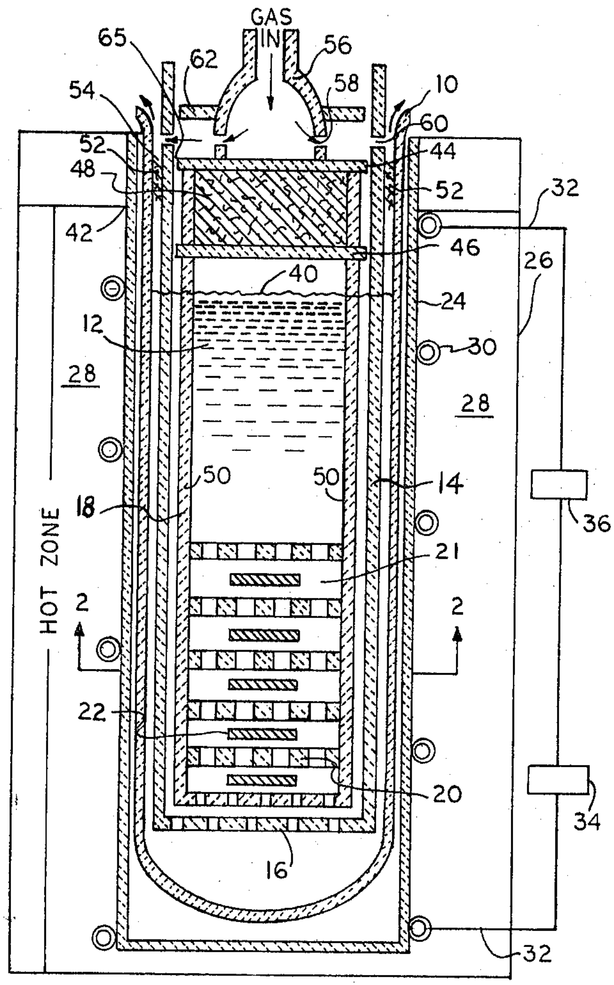


FIG. 1

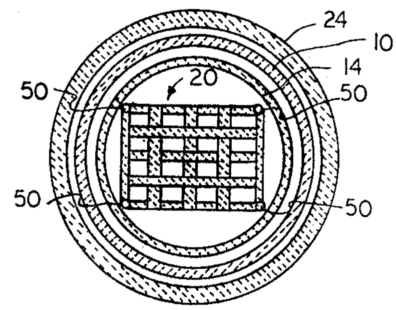


FIG. 2

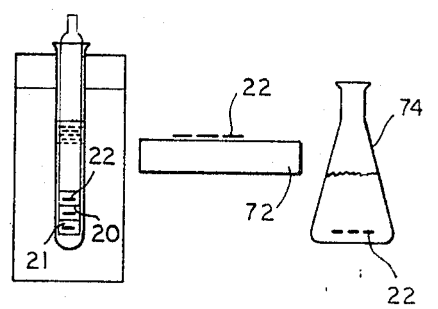


FIG. 4

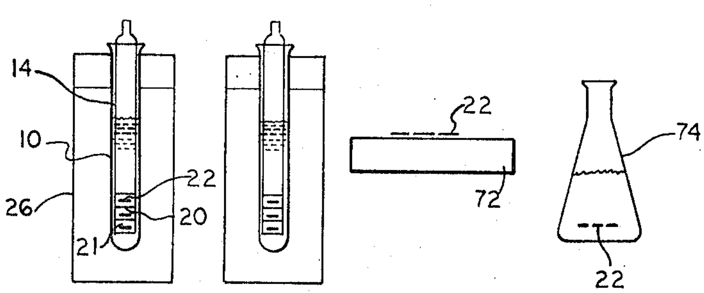


FIG. 3

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METHOD FOR PROCESSING SEMICONDUCTORS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to processing semiconductor materials. More particularly, this invention relates to an improved process and apparatus for treating semiconductors in a bath of molten material containing constituents reactive with the atmosphere.

2. Description of the Prior Art

Processing of semiconductors in many cases requires the controlled introduction or removal of certain types of constituent atoms from specimen slabs or chips. In liquid diffusion processing, the specimens or slabs are submerged in a molten treating environment at fairly high temperature. When the molten environment is reactive with the atmosphere, the specimens and treating material are sealed in a capsule.

In many cases the coefficient of expansion of the molten treating material differs markedly from that of the slabs or specimens and if the high melting point materials are not removed from the slabs before cooling, the slabs are crushed. In one generally practiced process, the specimens and treating material are sealed into a quartz capsule which is then heated in a horizontal furnace at a temperature above the melting point of the molten treating environment. After the diffusion step is complete, the capsule is tilted to expose the slabs and one end of the capsule is cooled to distill the remaining molten material from the surfaces of the specimen. Exposure of the surfaces of the specimens to a non-liquid environment during distillation can detrimentally affect the beneficial gettering effect of liquid submersion. The capsule must be broken to remove the specimens. Some specimens are not completely freed of the material and are crushed during cooling. Furthermore, the process is cumbersome and requires sacrificing quartz capsules with each run.

OBJECTS AND SUMMARY OF THE INVENTION

It is therefore an object of this invention to improve the procedure and apparatus for treating semiconductor materials in molten environments.

A further object of the invention is to provide an open crucible process for treating semiconductor materials.

Another object of the present invention is the provision of apparatus for simultaneously and conveniently treating multiple semiconductor specimens in a molten environment reactive with the atmosphere.

A still further object of this invention is to provide an improved process for removing high melting point materials from semiconductor specimens.

These and other objects and many attendant advantages of the invention will become apparent as the description proceeds.

The apparatus, according to the invention, includes an open vertical crucible means for receiving a charge of treating material. The crucible is received in a furnace having a vertical heating cavity. An open top liquid permeable carrier member is inserted into the container. The carrier contains a plurality of porous spacer means forming compartments for separating a plurality of treatable specimens. Means are provided for isolating the charge of molten material from the atmosphere. The isolating means can comprise inert materials such as particulate carbon placed on top of the molten charge of preferably a flow of inert gas can be provided across the upper portion of the crucible.

In the processing of specimens according to the invention a specimen is encased in each of the liquid permeable compartments provided within the carrier member. The carrier member is submerged in a body of molten treating material within the crucible. The body of molten material and carrier member are open to but isolated from the atmosphere. The carrier is readily removable from the treating material at the completion of the diffusion process. In another aspect of the treating process of specimens are submerged in a body of molten material which is a solvent for the treating material and has a melting temperature near room temperature, suitably no higher than 250° C. and preferably no more than about 150° C. The carrier member is then removed from the body of low melting material and the specimens placed on a hot plate and heated to the melting temperature of the low melting material thereby facilitating removal of the material from the surfaces of the specimen. The processing may be completed with cutting abrasion and etching of the low melting material.

The invention will now become better understood by reference to the following detailed description when considered in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a front view in section of an embodiment of the apparatus of the invention.

FIG. 2 is a sectional view taken on the line 2—2 of FIG. 1.

FIG. 3 is a schematic block diagram of a two-step process for treating donor-doped zinc sulfide crystals to render them more conducting; and

FIG. 4 is a schematic block diagram of a one-step process for treating donor-doped zinc sulfide crystals to render them more conducting.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring now to FIG. **1**, the semiconductor treating apparatus according to the invention, generally comprises an open system including a crucible **10** having a closed bottom and an open top for receiving a charge **12** of the treating material. The crucible **10** is suitably in the form of a cylindrical test tube. The carrier member is formed from an outer cylindrical holder **14** and an inner separator member **18**. The outer holder **14** has a liquid permeable bottom **16**. The inner member **18** contains a plurality of separated perforated shelves **20** supported on rods **50**. When the inner separator member **18** is inserted into the outer holder **14**, liquid permeable compartments **21** are formed between the shelves as horizontal walls and the inner surface of the holder **14** as the vertical wall thereof. The semiconductor specimens **22** are contained within the compartments **21**.

The treating apparatus is constructed of materials inert to the molten charge and to the specimens at the temperature of treatment. Pyrex is suitable for operating temperatures up to about 550° C., quartz for operating temperatures up to about 1,100° C. to 1,400° C. The apparatus can be constructed of graphite, vitreous carbon or other refractories such as boron nitride, alumina, zirconia or the like. During the diffusion treatment the crucible **10** is disposed within a vertical ceramic cylinder **24** of a crucible furnace **26**. The furnace contains a heating zone **28** provided by a heating coil **30** spirally wound around the ceramic cylinder **24**. The coil **30** is connected through electrical lead **32** to a source of potential **34** through a temperature control means **36**. The hot zone **28** extends from the bottom of the cylinder to a point above the level **40** of the molten charge of treating material, and suitably to a point **42** intermediate the two baffles **44** and **46**.

The baffles **44** and **46** are provided to decrease the flow of vapor out of the system. The compartment formed between the baffles **44** and **46** may be filled with a material **48** such as glass or quartz wool which can preferentially adsorb the vapors leaving the top of the melt **40**.

Referring now to FIGS. **1** and **2**, the baffles **44** and **46** are supported on four vertical rods **50** which are also attached to the corners of each shelf or spacer **20**. An additional portion of glass or quartz wool **52** may be inserted in the space **54** between the outer crucible **10** and the outer holder **14** of the carrier.

A gas inlet member **56** may be attached to the top baffle **44**, the inlet member **56** has a plurality of side openings **58** provided opposite similar openings **60** formed in the carrier member **14**. An upper baffle **62** may be provided on the inlet member **56** of the opening **60**.

In operating the apparatus according to the invention, the crucible **10**, outer holder **14** and separator member **18** are cleaned and dried. A set of specimens **22** are inserted into the compartment **21** formed between the porous shelves **20**. A wad **48** of glass or quartz wool is placed in the space between the baffles **44** and **46** and the carrier assembled by inserting the separator **18** into the holder **14**. The crucible **10** is inserted into the ceramic cylinder **24** and filled with a dry solid charge **12** of treating material. The temperature controller **36** is adjusted to heat the crucible **10** to a temperature to just above the melting temperature of the charge **12**. This minimizes the thermal shock to the specimens **22**. The crucible **10** is purged with inert gas. A gas line is connected to the gas inlet **56** and a slow flow of gas is initiated. The assembled carrier is then slowly inserted into the melted charge **12** within crucible **10**.

The temperature controller **36** is then set at a level to provide a temperature within crucible **10** intermediate the melting point and boiling point of the charge **12**. A further small portion of glass or quartz wool **52** is inserted into the space **54** between the crucible **10** and the outer holder **14**. The molten charge **12** will permeate through the liquid permeable bottom **16** of the holder **14** of the carrier member and through each of the porous spacer shelves **20** and will flow past the exposed surfaces of the specimens **22**. The specimens **22** are freely floating between the shelves **20** but are prevented from leaving the compartments **21** by the restraining walls of the surrounding holder member **14**.

The tendency of the vapors leaving the top of the molten charge **40** to rise through the system by convection forces and to flow towards an area of lower pressure is counteracted by several aspects of the apparatus of the invention. The hot zone **28** is terminated intermediate the baffles to impede the convection forces contributing to the rise of the vapors. The baffles **44** and **46** with the enclosed glass or quartz wool will provide a further restraint on the rise of gas. The low flow of inert gas provided through inlet **56** provides a slight pressure head above the system preventing escape of gas and further sweeps out any small amount of the vapor that does manage to rise to the top of the system. The gas flowing out the openings **58** in inlet **56** will scavenge any small amount of vapor escaping through the small clearance opening between baffle **44** and the holder **14**. The gas flow continues through openings **60** in holder **14** and will scavenge any gas rising between the holder **14** and the crucible **10**. However, the clearance between the baffles **44** and **46** and the carrier member **14** is maintained open so that the carrier **14** or the basket member **18** can readily be removed from the system even if some vapor rises and deposits in the clearance spaces **65** and **54**.

At the termination of the diffusion treatment or at any other stage of the processing, the carrier can be simply removed from the container **10** and delivered to another station for further processing. Another carrier member can be assembled with specimens and glass wool, during the diffusion treatment and can be inserted into the crucible **10** containing the molten charge for a next diffusion run during the further processing of the first one. After removal of the holder **14**, the molten charge **12** can be reduced in temperature to just above the melting point of the charge to reduce the thermal shock to the next run of specimens **22**.

One of the principal advantages of the apparatus and system of the invention is the ability to operate in an open system such that a plurality of specimens can readily be inserted or removed from a molten treating bath, thus avoiding operations in non-liquid environments. Furthermore, processing the specimens within a sealed capsule is obviated and breaking the capsule to extract the specimens is not necessary.

Other forms of apparatus can readily be substituted with similar advantages. For example, the porous compartments can take many shapes and forms. The compartments may be provided in a horizontal arrangement and may be cylindrical or other shape. The spacers need not be rigidly joined to the assembly but may be alternated between specimen members by sliding the specimens and spacers directly into the carrier member. The holder may be eliminated and the inner surface of the crucible may then serve the additional function of preventing the specimens from leaving the compartment formed between two shelves. The system may be run in essentially open condition without provision of an inert gas blanket above the charge. For example, an inert solid or liquid blanket may be floated directly on top of the charge **12**, suitably composed of an inert particulate high temperature refractory such as particulate carbon or a molten low vapor pressure material such as boron oxide. These and many other modifications will be readily apparent to those skilled in the art.

The apparatus of the invention is most useful in processes requiring molten treating charges which are reactive with the atmosphere. Another aspect of the apparatus is that the oxygen in the atmosphere is prevented from reaching and dissolving within the molten charge. This is very important with semiconductor materials, the properties of which are affected by dissolved oxygen.

For example, wide band gap semiconductors such as zinc sulfide are difficult to treat without the simultaneous introduction of defects or impurities which interfere with the electrical or luminescent properties of the material. For electronic devices the resistivity of zinc sulfide is preferably about 1 to 100 ohm-cm. so that there is a very small voltage drop across the body of material and ohmic contacts are relatively easier to form on lower resistivity material.

Zinc sulfide is most easily rendered N-type if a suitable donor atom such as a Group III metal like aluminum is substitutionally introduced into the material. The body of material may be in the form of a grown crystal or a film deposited onto a substrate.

The typical form of aluminum-doped zinc sulfide contains a donor level of about 100 p.p.m. which is sufficient to provide a free carrier concentration of approximately 10^{17} electrons per cubic centimeter if properly treated. However, the material, as grown, is in a high resistivity form because the aluminum donors have been compensated or complexed with another deep center, most probably a zinc vacancy. The zinc vacancy acts as an acceptor, single or double, and binds the extra electron present on the aluminum atom. Instead of the electron entering the conduction band, it is trapped. The presence of zinc vacancies is further evidenced by very bright emission of blue light, when the crystal is irradiated with ultra-violet photons.

In accordance with the prior art, the resistivity of the crystal specimen is lowered by treating the crystal in a molten zinc containing environment at high temperature for a period sufficient to diffuse zinc vacancies from the specimen. As previously discussed, since molten zinc is reactive with the atmosphere, this treatment was performed by sealing zinc sulfide slices in a capsule containing molten zinc and then tilting the capsule to expose the zinc sulfide crystals and distilling the remaining zinc from the specimen surface.

With the use of the apparatus of the invention, the zinc sulfide specimens need not be sealed in a capsule, the treating material is not distilled with specimen surfaces exposed to a non-liquid environment and the treatment is conducted in an open system providing much more convenient handling and processing of the specimens and with less breakage of equipment and specimens and much higher production of treated specimens per run.

In accordance with the invention, operation in a sealed environment is not required since the open crucible apparatus permits ready removal of the specimens from the molten environment before the zinc charge can solidify and crush the specimens and the processing according to the invention provides a simplified procedure for removing the molten environment under ambient conditions.

In accordance with the invention, a plurality of zinc sulfide specimens are immersed in a molten zinc containing charge heated to a temperature intermediate the melting point and boiling point of the charge and the specimens are treated for a period sufficient to diffuse zinc vacancies from the specimen.

After the diffusion treatment is terminated, the specimens are immersed in a molten body of low melting point material. The specimens are removed from the low melting material and the low melting material is removed from the surface of the specimens while maintaining the specimens at a temperature above the melting point of the low melting material. A low velocity flow of an inert gas such as argon may be flowed across the top of the molten zinc containing charge to prevent the atmospheric oxygen from reacting with the zinc vapor present above the change.

Referring now to FIG. 3, in a preferred treating process according to the invention, aluminum doped zinc sulfide specimens **22** loaded into a holder-separator carrier assembly **14, 18** are inserted into a crucible **10** filling with a molten body of pure zinc. For specimens **40-65** mils thick, sufficient zinc vacancies are diffused out of slices treated for one hour at **800°** C. It is apparent that the time and temperature of the treatment will be selected in accordance with the thickness of the slice.

After the diffusion treatment is terminated, the holder **14** is removed from the zinc bath and inserted into a second crucible **10** containing a lower melting point metal such as indium or gallium having a melting point preferably no greater than about 150° C. The bath is maintained at a temperature above the melting point of zinc, 420° C., so that the zinc dissolves rapidly and is removed from the surface of the specimens **22** and is replaced by the lower melting point soft metal.

After several minutes treatment at a temperature about 420° C., the holder member **14** is removed from the indium bath and the specimens removed from the shelves and delivered to a hot plate **72**. Since the melting point of indium is 156° C. the temperature differential between its melting point and room temperature is much smaller than zinc metal which melts at 420° C. and there will be less differential contraction. The hot plate is maintained at a temperature just above the melting point of indium while the soft indium is removed by wiping the surfaces of the specimen with a glass slide or glass wool. For final cleaning treatment, the specimens **22** may be mildly etched in an HCl etching bath **74** for several minutes to 1 hour.

In accordance with another embodiment of the invention, a single treatment in molten environment may be practiced by alloying the high melting treating metal with a low melting point metal such as indium or gallium. The low melting point alloying metal may be present in amounts from 10 to 90 percent by weight. With the use of such alloys, the boiling point of the treating bath is raised from about 907° C. for pure zinc to about 1,150° C. for a zinc-90 indium alloy. Furthermore, the melting point of indium is about 156° C. while that of its alloy with zinc is about 145° C.

Referring now to FIG. 4 the carrier is assembled by loading separator **18** with aluminum-doped zinc specimens **22** and inserting the separator **18** into the holder **14**. The assembled carrier is inserted into a crucible **10** charged with a 10 percent zinc-90 percent indium alloy which is then raised to 800° C., and maintained at that temperature for a selected period. The diffusion treatment is conducted as discussed with respect to FIG. 3 though the temperature could be raised up to about 1,150° C. The holder **14** is removed from the crucible **10** after termination of the diffusion treatment and then the specimens directly delivered to the hot plate **72** and rubbed with quartz wool to remove the remaining zinc-indium alloy. The hot plate is maintained at a temperature above 145° C. The specimens are then placed in container **74** and subjected to a mild HCl etch for about an hour.

It is to be realized that only preferred embodiments of the invention have been disclosed and that numerous substitutions alterations and modifications are all permissible without departing from the spirit and scope of the invention as defined in the following claims.

What is claimed is:

1. A method of diffusion treating semiconductors comprising the steps of:
- forming a stack of semiconductor slabs separated by liquid permeable spacers;
- inserting the stack into an open bath of molten treating material and diffusion treating the slabs therein;
- withdrawing the stack from the bath; and
- removing the remaining treating material from the surfaces of the slabs.

2. A method according to claim **1** in which a constituent of the bath is reactive with the atmosphere and further comprising the step of isolating the vapors of said bath constituent from the atmosphere.

3. A method according to claim **2** in which said vapors are isolated from the atmosphere by slowly flowing an inert gas across said bath.

4. A method according to claim **2** in which the semiconductor comprises zinc sulfide.

5. A method according to claim **4** in which the semiconductor comprises donor-doped zinc sulfide and the treating material comprises zinc.

6. A method according to claim **1** in which said stack is contained in a carrier member inserted into the open bath.

7. A method according to claim **1** in which said molten treating material is removed from the surfaces of the slabs by inserting the slabs in a bath of molten material having a lower melting point than the melting point of the treating material and replacing the treating material on the slabs with the lower melting point material.

8. A method according to claim **6** further comprising the step of withdrawing the slabs from the bath of lower melting point material and heating the slabs to a temperature above the melting point of the lower melting point material while mechanically removing the material from the surface of the slabs.

9. A method according to claim **7** in which the treating material and lower melting material is an alloy of said materials.

10. A method according to claim **7** in which the semiconductor comprises a wide band gap electro luminescent semiconductor compound and the treating material contains an atom of said compound.

11. A method according to claim **10** in which the compound is zinc sulfide.

12. A method according to claim **11** in which the compound is a Group III metal doped zinc sulfide and the treating material comprises zinc.

13. A method according to claim **9** in which the lower melting point material is selected from the group consisting of indium, gallium and alloys thereof.

14. A method according to claim **12** in which the lower melting material is indium.

15. In a process for diffusion treating semiconductor specimens in a molten body of high melting treating material the steps comprising:
- alloying said treating material with a lower melting material to form a treating bath having much lower melting point than said body of treating material;
- diffusion treating said specimens in an open molten bath of said alloyed treating material;
- removing the treated specimens from the open bath; and
- heating the specimens to a temperature above the melting point of said alloy while mechanically removing the alloy from the surfaces of the specimens.

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