

[54] **METHOD FOR DEPOSITING AN EPITAXIAL SEMICONDUCTIVE LAYER FROM THE LIQUID PHASE**

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[52] **U.S. Cl.**..... **148/171, 148/172, 148/1.5, 148/1.6, 118/401, 117/201, 23/273 SP, 23/301 SP**

[51] **Int. Cl.**..... **H011 7/38**

[58] **Field of Search**..... **148/171, 172, 1.5, 148/1.6, 401, 421; 117/201; 23/273 SP, 301 SP**

[56] **References Cited**

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Primary Examiner—G. T. Ozaki

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[57] **ABSTRACT**

An epitaxial layer of a semiconductive material is deposited on a substrate in a furnace boat having a well and a cup-shaped piston fitting in the well with the piston having a small hole in its top end. A heated solution of the semiconductive material dissolved in a molten metal solvent is provided in the well. The piston is pressed down against the solution to force some of the solution through the hole in the piston onto the top end of the piston. As the solution passes through the hole in the piston the solution is scraped clean of contaminants. The substrate is placed against the cleaned portion of the solution on the top end of the piston and the solution is cooled to deposit an epitaxial layer of the semiconductive material onto the substrate.

4 Claims, 6 Drawing Figures

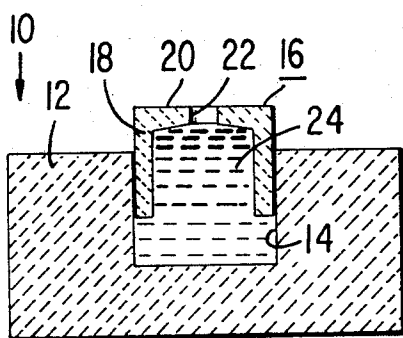


Fig. 1.

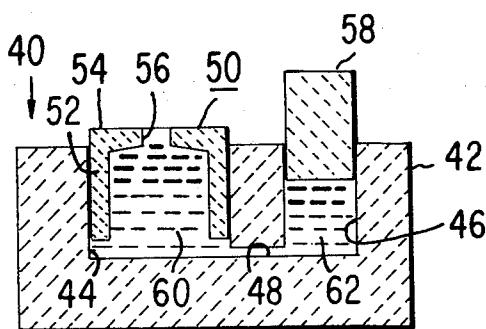


Fig. 4.

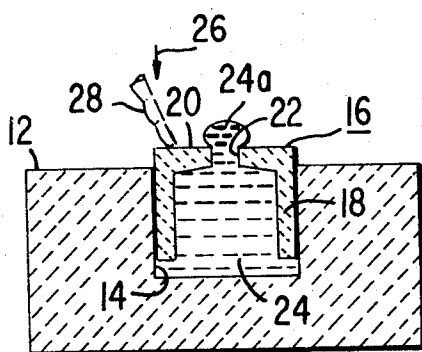


Fig. 2.

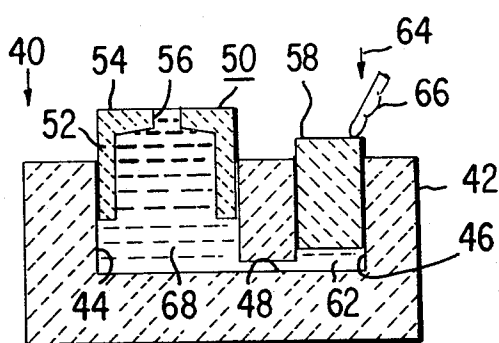


Fig. 5.

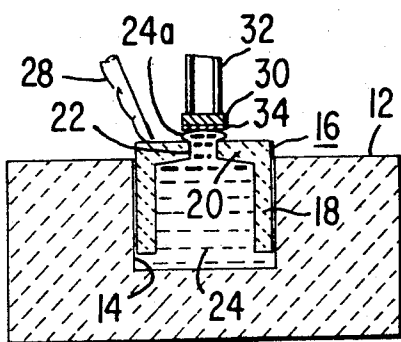


Fig. 3.

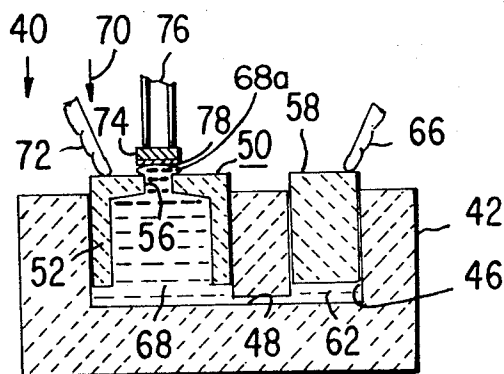


Fig. 6.

METHOD FOR DEPOSITING AN EPITAXIAL SEMICONDUCTIVE LAYER FROM THE LIQUID PHASE

BACKGROUND OF INVENTION

The present invention relates to the deposition of an epitaxial layer of a semiconductor material on a substrate from the liquid phase. More particularly, the present invention relates to a method and apparatus for depositing thin epitaxial layers from a liquid solution which has been scraped clean of contaminants.

Epitaxial layers of single crystalline semi-conductive material have been deposited on a crystalline substrate by contacting a surface of the substrate with a solution of a semiconductive material dissolved in a molten metal solvent; cooling the solution so that a portion of the dissolved semiconductive material precipitates and deposits on the substrate as an epitaxial layer; and then removing the solution from the substrate. This method is known as solution growth or liquid phase epitaxy. For a detailed description see H. Nelson, "Epitaxial Growth from the Liquid State and its Application to the Fabrication of Tunnel and Laser Diodes," RCA REVIEW 24, pg. 603, 1963. This technique has been found most suitable for depositing epitaxial layers of the group III-V semiconductive compounds, such as the phosphides, arsenides, antimonides of aluminum, gallium and indium and mixtures of such compounds.

In the use of this technique various problems have arisen. One problem is in the deposition of thin layers. When the solution is cooled to deposit an epitaxial layer on the substrate, the amount of the semiconductor material deposited per degree drop in temperature of the solution, which determines the thickness of the deposited layer per degree drop in the temperature, depends on the volume of the solution over the substrate. The greater the volume the more the semiconductive material deposited. Thus, to obtain a thin epitaxial layer with any degree of control it is desirable to use a small volume of the solution. However, because of the properties of the materials used for the solution it is difficult to obtain a small volume of the solution over the entire surface of a substrate.

Another problem which arises in epitaxial deposition from the liquid phase is that certain of the materials used, particularly aluminum, have a high affinity for oxygen and readily form an oxide. Even though this technique is generally carried out in a chamber through which a flow of a protective gas is passed, it is difficult to maintain the chamber completely oxygen free. Thus, when such oxygen affinity ingredients are included in the solution there is a tendency for oxides to be formed on the surface of the solution and such oxides interfere with the achievement of good epitaxial layers. Still another problem arises when depositing the mixed semiconductive compounds. If the ingredients are mixed together too far ahead of the actual deposition step, there may be a tendency for the premature formation of the compound in the solution rather than in the forming of the epitaxial layer. Therefore, it would be desirable to be able to mix the ingredients together just prior to the beginning of start of the epitaxial deposition so as to prevent the premature formation of the compound.

An epitaxial layer of a crystalline material is deposited on a substrate by forming in a well of a furnace boat a solution of the material in a molten solvent. The solution is forced through a hole in a wall extending

over the well so as to provide a glob of the solution on the wall with the glob having been mechanically scraped of surface contaminants. A substrate is brought into contact with the glob of the solution so that the glob extends in contact with a surface of the substrate. The solution is cooled to precipitate some of the crystalline material in the glob of the solution and deposit the crystalline material on the surface of the substrate as an epitaxial layer. The substrate with the epitaxial layer thereon is then removed from the glob of the solution.

BRIEF DESCRIPTION OF THE DRAWING

FIGS. 1-3 are sectional views of one form of the apparatus of the present invention at various stages of the method of the present invention.

FIGS. 4-6 are sectional views of another form of the apparatus of the present invention at various stages of the method of the present invention.

DETAILED DESCRIPTION

Referring initially to FIG. 1, one form of the apparatus of the present invention is generally designated as 10. The apparatus 10 comprises a furnace boat 12 of a refractory material, such as graphite, having a well 14 in its top surface. A hollow cup-shaped piston 16 of a refractory material, such as graphite, fits in the well 14. The outer wall 18 of the piston 16 is of a size and shape to have a close sliding fit within the well 14. The top end wall 20 of the piston 16 has a small hole 22 therethrough. The piston 16 fits in the well 14 with the open end of the piston being within the well and the top end wall 20 of the piston extending across the open end of the well.

To carry out the method of the present invention with the apparatus 10, a charge is placed in the well 14 and the piston 16 is placed in the well 14 over the charge. The charge is a mixture of the semiconductive material of the epitaxial layer to be deposited, a metal solvent for the semiconductive material and, if the epitaxial layer is to be of a particular conductivity type, a conductivity modifier. For example, to deposit an epitaxial layer of gallium arsenide, the semiconductive material would be gallium arsenide; the metal solvent could be gallium; and the conductivity modifier could be either tellurium or tin for an N type layer or zinc, germanium or magnesium for a P type layer. The semiconductive material and the conductivity modifiers are generally present in granulated solid form at room temperature. Since certain of the metal solvents which can be used, such as gallium, have a melting temperature close to room temperature, the melting temperature of gallium being about 30°C, the metal solvent may be present either in granulated solid form or in liquid form depending on the ambient temperature where the method is being carried out.

The loaded furnace boat 12 is then placed in a furnace chamber (not shown) having a heating means, such as a resistance heater, on which the boat is seated. The chamber should also include manipulators for carrying out operations within the chamber from outside the chamber and a window for observation and illumination. A flow of a protective or reducing gas, such as hydrogen or a hydrogen and nitrogen mixture, is provided through the furnace chamber and over the furnace boat 12. The heating means for the furnace chamber is turned on to heat the contents of the furnace boat

12 to a temperature at which the metal solvent is molten and the semiconductive material and conductivity modifiers dissolve in the molten metal solvent, for example between 800°C and 950°C for gallium arsenide and gallium aluminum arsenide. Thus, the charge becomes solution 24 of the semiconductive material and the conductivity modifiers in the molten metal solvent. The quantity of the charge placed in the well 16 is sufficient such that when the solution 24 is formed, the piston 16 will float on the solution with the bottom open end of the piston being spaced from the bottom of the well 14, as shown in FIG. 1.

The piston 16 is then pressed downwardly into the well 14 as indicated by the arrow 26 in FIG. 2. As shown in FIG. 2, this can be accomplished by a stylus 28 attached to one of the manipulators of the furnace chamber. Pressing the piston 16 downwardly into the well 14 causes some 24a the solution 24 to be squeezed through the hole 22 in the top wall with the piston to provide This glob 24a of the solution on the top wall 20. As the solution is squeezed through the hole 22 any oxides or connected contaminants on the surface of that solution are mechanically scraped from the surface of the solution so that a fresh, the tube. free glob 24a of the solution is provided on the top wall 20 of the piston. the deposition

As shown in FIG. 3, a flat substrate 30 of a material suitable for epitaxial deposition is then placed against the glob 24a of the solution so that the glob 24a is in contact with a surface of the substrate. This is achieved by supporting the substrate 30 on the end of a suction tweezer 32, which is a tube mounted on a manipulator and connected to a vacuum pump, so that the substrate is held against the end of the tube by the suction through the tube. By lowering the suction tweezer 32, the surface of the substrate 30 is pushed against the glob 24a of the solution until the solution is spread out across the surface of the substrate. The temperature of the heating means is then lowered so as to cool the solution 24. Cooling the solution 24 causes some of the semiconductive material in the glob 24a of the solution to precipitate and deposit on the surface of the substrate 30 to form an epitaxial layer 34. During the deposition of the semiconductive material some of the conductivity modifiers in the solution becomes incorporated in the lattice of the epitaxial layer 34 to provide the epitaxial layer with a desired conductivity type. Since the glob 24a of the solution which is in contact with the substrate 30 is of small volume, a thin epitaxial layer 34 can be easily deposited. The suction tweezer 32 is then lifted upwardly to move the substrate 30 with the epitaxial layer 34 thereon out of contact with the solution. Thus, there is provided a method and apparatus wherein a thin epitaxial layer can be easily deposited from a liquid solution which has been cleaned of oxides or other surface contaminants.

Referring to FIG. 4, another form of the apparatus of the present invention is generally designated as 40. The apparatus 40 comprises a furnace boat 42 of a refractory material, such as graphite, having first and second spaced wells 44 and 46 in its top surface. The wells 44 and 46 are connected together adjacent their bottoms by a small passage 48. A hollow, cup-shaped piston 50 of a refractory material is within the first well 44. The outer wall 52 of the piston 50 is of a size and shape to have close sliding fit within the first well 44. The top end wall 54 of the piston 50 has a small hole 56 there-

through. The piston 50 fits in the first well 44 with the open end of the piston being within the well and the top end wall 54 extending across the open end of the well. A solid piston 58 of a refractory material is within the second well 46. The solid piston 58 is of a size and shape to have sliding fit within the second well 46.

To carry out the method of the present invention with the apparatus 40, a separate charge is placed in each of the first and second wells 44 and 46. The hollow piston 50 is placed over the charge in the first well 44 and the solid piston 58 is placed over the charge in the second well 46. Each of the charges in the wells includes a metal solvent, such as gallium. However, the other ingredients which are to make up the final deposition solution are separated between the two charges. For example, if the semiconductive material to be deposited is a mixed group III-V semiconductive compound, such as gallium aluminum arsenide or gallium aluminum phosphide, the ingredients which are used to form the mixed semiconductive material compound are separated between the two charges. For example, for depositing either gallium aluminum arsenides or gallium aluminum phosphide, the gallium arsenide or gallium phosphide can be included in the charge in the first well 44 and the aluminum in the charge in the second well 46. A conductivity modifier may be included in either or both of the charges.

The loaded furnace boat 42 is then placed in a furnace chamber (not shown) of the same type previously described with regard to the furnace boat 10 of FIG. 1. A flow of a protective or reducing gas is provided through the furnace chamber and over the furnace boat 42. The heating means for the furnace chamber is turned on to heat the contents of the furnace boat 42 to a temperature at which the metal solvent is molten and the other ingredients of the charges will dissolve in the molten metal solvent. Thus, the first charge becomes a first solution 60 of the molten metal solvent having the other ingredients of the charge dissolved therein and the second charge becomes a second solution 62 of the molten metal solvent having the other ingredients of the charge dissolved therein.

As shown in FIG. 5, the solid piston 58 is then pushed downwardly into the second well 46 as indicated by the arrow 64 by means of a stylus 66 which is attached to one of the manipulators of the furnace chamber. This forces some of the second solution 62 through the passage 48 into the first well 44 where it mixes with the first solution 60. The mixing of the first and second solutions 60 and 62 forms in the first well 44 the deposition solution 68 having the desired ingredients. Thus, if the first solution 60 contained either gallium arsenide or gallium phosphide and the second solution 62 contained aluminum, the deposition solution will contain either gallium arsenide and aluminum to deposit gallium aluminum arsenide or gallium phosphide and aluminum to deposit gallium aluminum phosphide.

As shown in FIG. 6, the hollow piston 50 is then pressed downwardly into the first well 44 as indicated by arrow 70 by means of a stylus 72 attached to a manipulator of the furnace chamber. This causes some of the deposition solution 68 to be squeezed through the hole 56 in the top wall 54 of the hollow piston 50 to provide a small glob 68a of the deposition solution on the top wall 56. As the deposition solution 68 is squeezed through the hole 56 it is mechanically scraped clean of any surface oxides or other contami-

nants so that so as to provide a fresh, oxide free glob 68a of the solution on the top wall 54 of the piston 50. A substrate 74 mounted on the end of a suction tweezer 76, which is secured to a manipulator of the furnace chamber, is lowered against the glob 68a of the deposition solution so that the solution is spaced across and is in contact with a surface of the substrate. The temperature of the heating means for the furnace chamber is lowered so as to cool the deposition solution 68. This causes some of the semiconductive material in the glob 68a of the deposition solution to precipitate and deposit on the surface of the substrate to form an epitaxial layer 78. During the deposition of the semiconductor material some of the conductivity modifiers in the deposition solution becomes incorporated in the lattice of the epitaxial layer 78 to provide an epitaxial layer of a desired conductivity type. The suction tweezer 76 is then lifted to move the substrate 74 with the epitaxial layer 78 thereon out of contact with the deposition solution. Thus, with the apparatus 40 a thin epitaxial layer can be easily deposited from a liquid solution which has been cleaned of surface oxide or other contaminants. In addition, the apparatus 40 permits the mixing of the ingredients of the material to be deposited just prior to the starting of the actual deposition so as to minimize the possibility of premature formation of the material in the deposition solution.

We claim:

1. A method of depositing an epitaxial layer of a crystalline material on the surface of a substrate comprising the steps of:

- a. forming in the well of a furnace boat a deposition solution of a material dissolved in a molten solvent,
- b. forcing some of said deposition solution through a

hole in a wall extending over the well so as to provide a glob of said deposition solution on said wall with the glob having been mechanically scraped of surface contaminants,

- c. bringing a substrate into contact with said glob of the solution so that the glob extends in contact with a surface of the substrate,
- d. cooling said solution to precipitate some of the crystalline material from said glob of the solution and deposit said semiconductive material on the surface of the substrate as an epitaxial layer, and
- e. removing said substrate with the epitaxial layer thereon from the glob of the solution.

2. The method in accordance with claim 1 in which the solution is forced through the hole in the wall by pressing the wall against the solution.

3. The method in accordance with claim 1 in which the deposition solution is formed by forming a first solution in said well and a second solution in a second well in said furnace boat, said first solution comprising a molten solvent having dissolved therein some of the ingredients of the material to be deposited, said second solution comprising a molten solvent having dissolved therein other ingredients of the material to be deposited and then mixing at least some of the second solution with the first solution to form the deposition solution.

4. The method in accordance with claim 3 in which the second solution is mixed with the first solution by forcing at least some of the second solution from the second well into the first well through a passage extending through the furnace boat between said wells.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,755,011 Dated August 28, 1973

Inventor(s) H. P. Kleinknecht & A. H. Oberholzer

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 18,	change "24a" to --of--;
line 19,	after "wall" insert --20--;
line 20,	change "This" to --a small--;
line 22,	change "connected" to --other--;
line 24,	change "the tube." to --oxide--;
line 26,	delete --the deposition--.

Column 4, line 5, change "6" to --46--.

Signed and sealed this 18th day of December 1973.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

RENE D. TEGTMEYER
Acting Commissioner of Patents