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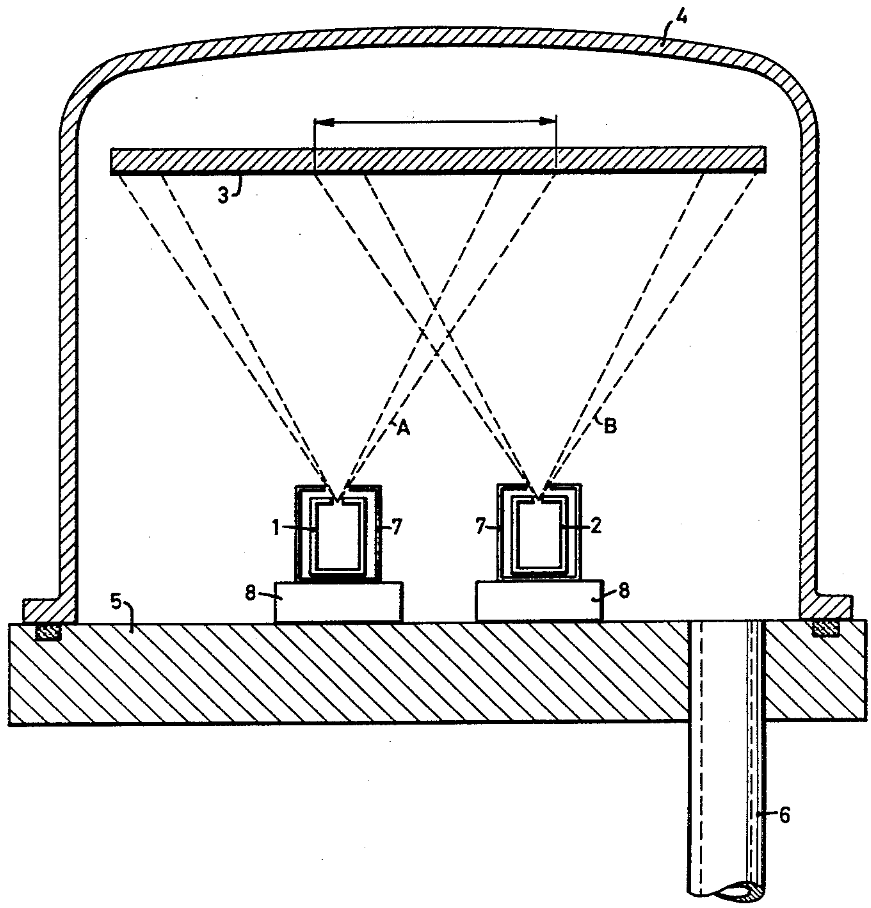

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VAPORIZATION METHOD OF PRODUCING THIN LAYERS OF SEMICONDUCTING COMPOUNDS

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22 Claims. (Cl. 117—212)

This invention relates to the production of thin layers or coatings from semiconducting substances. It particularly relates to the production, on a carrier surface, of a thin layer of multi-component substance, such as a semiconductor compound or alloy, by a process involving vaporization of the compounds. It especially relates to production of such a layer from a semiconductor compound which is composed of component elements that differ considerably in their respective partial vapor pressures above a melt of the compound.

Semiconducting layers, such as are used for example in electric, photoelectric or optical devices, may consist of semiconducting elements such as germanium, or they may consist of semiconducting alloys, or of compounds such as indium arsenide and antimonide, indium phosphide, gallium arsenide, gallium phosphide, and others. When semiconducting layers are to be prepared from elemental substances, they can be produced simply by vaporizing the element in vacuum onto a carrier. However, the production of thin layers, by vaporization, encounters difficulties when the layer is to consist of a semiconducting compound, particularly a compound whose constituents above the melt of the compound have considerably different vapor pressures. This applies particularly to some of the so-called $A_{III}B_{V}$ compounds, i.e. compounds formed of an element from the third group (boron, aluminum, gallium, indium) of the periodic system with an element from the fifth group (nitrogen, phosphorus, arsenic, antimony). These substances are: BN, BP, BAs, AlN, AlAs, AlSb, GaN, GaP, GaAs, GaSb, InN, InP, InAs and InSb. Also, coatings of $A_{II}B_{VI}$ semiconductor compounds can be produced by the method of the present invention, viz., mercury telluride.

An object of this invention is to overcome these difficulties and to provide a method which readily permits the production of thin layers by vaporization from those semiconducting compounds whose constituents above the melt exhibit considerably different amounts of vapor pressure.

To this end, and in accordance with my invention, the carrier or recipient surface which is to receive the vaporization-deposited layer of the compound is kept, during the vaporization process, at a temperature which is between the condensation temperature of the constituent of higher volatility, on the one hand, and the condensation temperatures of the constituent of lesser volatility and of the compound on the other hand. Furthermore, the density of the beam of vapor impinging upon the recipient is advantageously so rated as to provide in front of the recipient an excess of the constituent of higher volatility.

The invention will be further explained with reference to the drawing which illustrates, schematically, a device for performing the method.

In the drawing, two vaporizer vessels denoted by **1** and **2** are provided from which the constituents A and B respectively are vaporized onto a recipient or a preferably flat planar carrier sheet **3** in order to form thereon a semiconducting layer consisting of the compound AB. The entire device is located within a vacuum vessel **4**. The vessel **4** is disposed upon or fixed to a base plate **5** having a suction conduit **6** connected therein. Shown at **7** are the heating devices for evaporator vessels **1** and **2**. Heaters **7** are mounted upon the ceramic bases **8**. The heaters **7** comprise cylinder-shaped incandescent sheet metal members. The effective receiving area of the carrier **3**, in which the compound is to be produced, is located within the common or overlapping impinging range of both component vapor beams and is identified on the drawing by a double-headed arrow. The vapor beams A and B may have their axes parallel to each other or inclined toward each other. Beam A may be adjusted asymmetrically, if desired, to accentuate or to modify the decrease in impinging density on surface **3**, from the left to the right, in the overlapped portion. The apertures of the vessels **1** and **2** can be circular or transverse parallel slits.

For example, if a semiconductor layer of indium arsenide (InAs) is to be produced on carrier **3** by vaporization, then the vessels **1** and **2** contain the component substances As and In respectively. Both vessels are heated, so that the components contained therein are vaporized through an opening of the vessel toward the recipient **3**. The recipient **3** in this case is heated to a temperature of approximately 200° C. This temperature is below the condensation temperatures of the less volatile In component and of the compound InAs. But it is higher than the condensation temperaturre of the more volatile As component, on the basis of an impinging density of the As vapor beam of between 10^{17} to 10^{18} molecules per square centimeter per second. As a result of this selection of parameters, the entire In vapor flow condenses on the recipient. With the said conditions, if the In vapor flow were not present, the As vapor beam would be completely reflected. In the present case, however, the incoming As molecules form, together with the In molecules, the compound InAs, which likewise condenses on the recipient, to an extent predetermined by the number of the In molecules present in the beam. The excessive As molecules are reflected back into the vapor space.

It is advantageous that the pressure in the vacuum vessel be not greater than 10^{-5} mm. Hg, generally. At such a pressure, the incorporation of foreign gas atoms into the semi-conductor layer is negligibly small. Tests made with a still lower residual gas pressure exhibited only a slight improvement in the quality of the layer.

In order to make certain that the above-described method results in a stoichiometric layer of the compound, the impinging densities of the vapor beams of the respective components should not depart from each other to an indefinite or indiscriminate extent. That is, if in the above-described example the impinging density of the As vapor beam is too much larger than the impinging density of the In vapor beam, then a mechanical effect occurs consisting in the fact that the As molecules are covered by the condensing InAs. As a result, there occur inclusions of As which may have detrimental effect upon the properties of the semiconducting layer thus produced by vaporization. On the other hand, the most favorable ratio of the impinging densities of the component vapors is not always easy to control in technological application. This is particularly so if the differences in vapor pressure of the respective components are particularly great, as is the case with the above-mentioned InAs. In such cases, and in accordance with another feature of my invention, the geometric arrangement of the two vaporizer vessels relative to the recipient is so chosen that the impinging densities of the two component vapor beams vary along the recipient in mutually opposed sense. By way of example, this requirement can be satisfied by the above described arrangement illustrated on the drawing. The impinging density of the vapor beam issuing from the vessel 1 decreases from the left toward the right relative to the effective recipient area designated by the double-headed arrow. Inversely, the vapor beam issuing from the vessel 2 decreases in the opposite direction, namely from the right toward the left as far as the effective area of the recipient is concerned. This effect occurs because of the fact that the center of each vapor beam has a higher vapor density than the fringes, the center being closer to the source. Within the entire range, designated above as the effective area of the recipient, there will now occur a partial range in which a favorable ratio of the two impinging densities of the respective vapor beams obtains. This partial range is subsequently cut out of the entire area for later use of the vaporization-produced compound layer.

The manufacture of vaporized layers according to the present invention is generally advantageously carried out with the following further considerations in mind. The determined or selected entering density of the vapor of the less volatile component, for example, of the indium in the manufacture of layers of InAs, InSb and InP, or of the gallium in the manufacture of layers of GaAs or GaP, is such that the layers can be built up in a thickness of a few microns within a few minutes. This requires impinging densities of 10^{17} to 10^{18} particles per second and per $cm.^2$. The required vaporizing temperatures are determined by the vapor-pressure curves of the respective elements. For example, with indium one needs temperatures of 900° C. to 1000° C., depending upon the geometric arrangement. The temperature of the vaporizer containing the more volatile component, for example arsenic or antimony, is chosen so that the impinging density thereof, at the recipient, is preponderant relative to the impinging density of the less volatile component. The magnitude of this excess in density may vary between about twice and ten times the impinging density of the less volatile component. For example, with arsenic, temperatures between 300° C. and 350° C. and, with antimony, temperatures between 700° C. and 800° C. are applicable.

The temperature of the recipient surface 3 is kept below the melting temperature of the compound to be used and also below the vaporizing temperature of the more volatile component above the compound. The recipient temperature, in the manufacture of InAs and GaAs, is between 200 and 700° C. In the manufacture of InSb, the recipient temperature is between 400 and 530° C. Advantageously, the recipient 3 is a substance whose thermal coefficient of expansion is, as far as possible, coincident with that of the compound to be produced. In the manufacture of InAs and InSb, sintered corundum, manganese ferrite, zinc ferrite or hard glasses are suitable.

The layer thicknesses of the vaporization-deposited compounds generally lie between 1 micron and 5 microns.

The application of the procedure of the above example to the other compounds listed above, such as, for example, indium antimonide, indium phosphide, gallium arsenide and gallium phosphide, is self-evident. It involves the selection of specific physical parameters in accordance with the principle of the invention described above.

According to a further feature of my invention, relating to cases in which extremely accurate stoichiometry is desired, the vapor-deposited layer is tempered within the vapor of the component of higher volatility at a temperature closely below the melting temperature of the compound; and the vapor pressure of the component of higher volatility is so dimensioned or chosen as to be below the vapor pressure of the pure component of higher volatility but is higher than the corresponding vapor pressure above the stoichiometric compound at the tempering temperature. This has the effect that any particles of the low-volatile component that may be mechanically occluded in the vapor-deposition area will vaporize out of this area because the vapor pressure of such particles closely below the melting temperature of the compound is considerably higher than the partial vapor pressure of this component above the compound. If the occlusions of the low-volatile component are not excessively large, an equilibrium will thus adjust itself which strictly corresponds to the stoichiometry of the compound.

The tempering temperature chosen is such that decomposition of the compound does not yet occur, nor return vaporization of the low-volatile component out of the layer. Detrimental gases or vapors are absent.

With InAs, it is advisable to use a tempering temperature of 700° C. at an arsenic vapor pressure of 10^{-3} mm. Hg. Under these conditions, there is practically no return vaporization of the arsenic out of the InAs layer. A condensation of pure arsenic out of the layer cannot occur because the vapor pressure of arsenic, i.e. the "pure component," at 700° C., is several orders of magnitude higher. The vapor pressure above the "pure component" is also designated as "saturated vapor pressure" in contrast to the partial vapor pressure of this component above the compound.

With InSb, the tempering is performed between 500 and 530° C. in an antimony atmosphere of 10^{-3} mm. Hg.

I claim:

1. A method for producing a thin semiconductor layer of a semiconducting compound whose components, in molten condition, have different vapor pressures respectively, comprising simultaneously directing vapor beams of the components onto a carrier surface, the carrier surface being at a temperature between the condensing temperature of the component of higher volatility, on the one hand, and the condensing temperatures of the component of lower volatility and of the compound on the other hand, the impinging density of the vapor beam of the component of higher volatility on said surface being such as to maintain at the carrier surface a stoichiometric excess of the component of higher volatility.

2. The method of claim 1 in which the semiconductor is a semiconductor compound taken from the group consisting of boron nitride, boron phosphide, boron arsenide, aluminum nitride, aluminum arsenide, aluminum antimonide, gallium nitride, gallium phosphide, gallium arsenide, gallium antimonide, indium nitride, indium phosphide, indium arsenide, and indium antimonide, of the respective formulas BN, BP, BAs, AlN, AlAs, AlSb, GaN, GaP, GaAs, GaSb, InN, InP, InAs, and InSb.

3. The method of claim 1 in which the semiconductor compound is indium arsenide, of the formula InAs.

4. The method of claim 1 in which the semiconductor compound is indium arsenide, of the formula InSb.

5. The method of claim 1 in which the semiconductor compound is indium phosphide, of the formula InP.

6. The method of claim 1 in which the semiconductor compound is gallium arsenide, of the formula GaAs.

7. The method of claim 1 in which the semiconductor compound is gallium phosphide, of the formula GaP.

8. A method for producing a semiconductor layer of a semiconducting compound whose components, in molten condition, have different vapor pressures respectively, comprising simultaneously directing vapor beams of the components onto a carrier surface, the carrier surface being at a temperature between the condensing temperature of the component of higher volatility, on the one hand, and the condensing temperatures of the component of lower volatility and of the compound on the other hand, the impinging density of the vapor beam of the component of higher volatility on said surface being such as to maintain at the carrier surface a stoichiometric excess of the component of higher volatility, the vapor beams comprising two peripherally overlapping beams, the impinging density, namely molecules per square centimeter of carrier surface per second, of the overlapping portions decreasing along the carrier toward each other.

9. The method of claim 8 in which the semiconductor is a semiconductor compound taken from the group con-

sisting of boron nitride, boron phosphide, boron arsenide, aluminum nitride, aluminum arsenide, aluminum antimonide, gallium nitride, gallium phosphide, gallium arsenide, gallium antimonide, indium nitride, indium phosphide, indium arsenide, and indium antimonide, of the respective formulas BN, BP, BAs, AlN, AlAs, AlSb, GaN, GaP, GaAs, GaSb, InN, InP, InAs, and InSb.

10. A method for producing a thin semiconductor layer of a semiconducting stoichiometric compound whose components, in molten condition, have different vapor pressures respectively, comprising simultaneously directing vapor beams of the components onto a carrier surface, the carrier surface being at a temperature between the condensing temperature of the component of higher volatility, on the one hand, and the condensing temperatures of the component of lower volatility and of the compound on the other hand, the impinging density of the vapor beam of the component of higher volatility on said surface being such as to maintain at the carrier surface a stoichiometric excess of the component of higher volatility, and tempering the vaporization-deposited layer in the vapor of the component of high volatility at a temperature close to but below the melting temperature of the compound, the vapor pressure of the component of higher volatility, in the tempering, being lower than the vapor pressure of the pure component of higher volatility but higher than the vapor pressure of this component above the stoichiometric compound at the tempering temperature.

11. A method for producing a thin semiconductor layer of a binary semiconducting compound whose component elements, in molten condition, have different vapor pressures respectively, comprising simultaneously directing two partially overlapping diverging vapor beams of the components onto a carrier surface, the carrier surface being at a temperature between the condensing temperature of the component element of higher volatility, on the one hand, and the condensing temperatures of the component element of lower volatility and of the compound on the other hand.

12. A method for producing a thin semiconductor layer of indium arsenide of the formula InAs, comprising simultaneously directing two diverging vapor beams, of arsenic and indium respectively, onto a carrier surface, the beams partially overlapping thereon, the carrier surface being at a temperature above the condensing temperature of the arsenic and below the condensing temperatures of the indium and of the said indium arsenide compound, the impinging density of the vapor beam of the arsenic on said surface being such as to maintain at the carrier surface a stoichiometric excess of the arsenic, and subsequently cutting out, for use in semiconductor devices, at least part of only the area of the carrier surface impinged by the overlapping portions of the beam.

13. A method for producing a thin semiconductor layer of indium antimonide of the formula InSb, comprising simultaneously directing two diverging vapor beams, of antimony and indium respectively, onto a carrier surface, the beams partially overlapping thereon, the carrier surface being at a temperature above the condensing temperature of the antimony and below the condensing temperatures of the indium and of the said indium antimonide compound, the impinging density of the vapor beam of the antimony on said surface being such as to maintain at the carrier surface a stoichiometric excess of the antimony, and subsequently cutting out, for use in semiconductor devices, at least part of only the area of the carrier surface impinged by the overlapping portions of the beam.

14. A method for producing a thin semiconductor layer of indium phosphide of the formula InP, comprising simultaneously directing two diverging vapor beams, of phosphorus and indium respectively, onto a carrier surface, the beams partially overlapping thereon, the carrier surface being at a temperature above the condensing temperature of the phosphorus and below the condensing temperatures of the indium and of the said indium phosphide compound, the impinging density of the vapor beam of the phosphorus on said surface being such as to maintain at the carrier surface a stoichiometric excess of the phosphorus, and subsequently cutting out, for use in semiconductor devices, at least part of only the area of the carrier surface impinged by the overlapping portions of the beam.

15. A method for producing a thin semiconductor layer of gallium arsenide of the formula GaAs, comprising simultaneously directing two diverging vapor beams, of arsenic and gallium respectively, onto a carrier surface, the beams partially overlapping thereon, the carrier surface being at a temperature above the condensing temperature of the arsenic and below the condensing temperatures of the gallium and of the said gallium arsenide compound, the impinging density of the vapor beam of the arsenic on said surface being such as to maintain at the carrier surface a stoichiometric excess of the arsenic, and subsequently cutting out, for use in semiconductor devices, at least part of only the area of the carrier surface impinged by the overlapping portions of the beam.

16. A method for producing a thin semiconductor layer of gallium phosphite of the formula GaP, comprising simultaneously directing two diverging vapor beams of phosphorus and gallium respectively, onto a carrier surface, the beams partially overlapping thereon, the carrier surface being at a temperature above the condensing temperature of the phosphorus and below the condensing temperatures of the gallium and of the said gallium phosphide compound, the impinging density of the vapor beam of the phosphorus on said surface being such as to maintain at the carrier surface a stoichiometric excess of the phosphorus, and subsequently cutting out, for use in semiconductor devices, at least part of only the area of the carrier surface impinged by the overlapping portions of the beam.

17. A method for producing a thin semiconductor layer of a semiconducting compound whose components, in molten condition, have different vapor pressures respectively, comprising simultaneously directing vapor beams of the components onto a carrier surface, the carrier surface being at a temperature between the condensing temperature of the component of higher volatility, on the one hand, and the condensing temperatures of the component of lower volatility and of the compound on the other hand, the impinging density of the vapor beam of the component of higher volatility on said surface being such as to maintain at the carrier surface a stoichiometric excess of the component of higher volatility, and tempering the vaporization-deposited layer in the vapor of the component of high volatility at a temperature below the melting temperature of the compound.

18. A method for producing a thin semiconductor layer of the compound indium arsenide, of the molecular formula InAs, comprising simultaneously directing at least partially overlapping diverging vapor beams of arsenic and indium onto a carrier surface, the carrier surface being at a temperature between the condensing temperature of the arsenic vapor, on the one hand, and the condensing temperatures of the indium vapor and of the said compound, on the other hand, the impinging density of the vapor beam of the arsenic on said surface being such as to provide at the carrier surface a stoichiometric excess of said arsenic, said carrier temperature being 200° to 700° C.

19. A method for producing a thin semiconductor layer of indium antimonide of the molecular formula InSb, comprising simultaneously directing two diverging vapor beams, of antimony and indium, respectively, onto a carrier surface, the beams at least partially overlapping thereon, the carrier surface being at a temperature above the condensing temperature of the antimony vapor and below the condensing temperatures of the indium vapor

and of the said indium antimonide compound, the impinging density of the vapor beam of the antimony on said surface being such as to maintain at the carrier surface a stoichiometric excess of the antimony, the carrier temperature being about 400° to 530° C.

20. A method for producing a thin semiconductor layer of the compound indium arsenide, of the molecular formula InAs, comprising simultaneously directing at least partially overlapping diverging vapor beams of arsenic and indium onto a carrier surface, the carrier surface being at a temperature between the condensing temperature of the arsenic vapor, on the one hand, and the condensing temperatures of the indium vapor and of the said compound, on the other hand, the impinging density of the vapor beam of the arsenic on said surface being such as to provide at the carrier surface a stoichiometric excess of said arsenic, said carrier temperature being 200° to 700° C., and thereafter tempering the layer at about 700° C. at an arsenic vapor pressure of about 10^{-3} mm. of mercury.

21. A method for producing a thin semiconductor layer of the compound indium arsenide, of the molecular formula InAs, comprising simultaneously directing at least partially overlapping diverging vapor beams of arsenic and indium onto a carrier surface, the carrier surface being at a temperature between the condensing temperature of the arsenic vapor, on the one hand, and the condensing temperatures of the indium vapor and of the said compound, on the other hand, the impinging density of the vapor beam of the arsenic on said surface being such as to provide at the carrier surface a stoichiometric excess of said arsenic, said carrier temperature being 200° to 700° C., and thereafter tempering the layer in an atmosphere of arsenic vapor at a temperature close

to but below the melting temperature of the indium arsenide, the arsenic vapor in the tempering being at a vapor pressure lower than the vapor pressure of arsenic at the tempering temperature, but higher than the vapor pressure of arsenic above indium arsenide at said temperature.

22. A method for producing a thin semiconductor layer of indium antimonide of the molecular formula InSb, comprising simultaneously directing two diverging vapor beams, of antimony and indium, respectively, onto a carrier surface, the beams at least partially overlapping thereon, the carrier surface being at a temperature above the condensing temperature of the antimony vapor and below the condensing temperatures of the indium vapor and of the said indium antimonide compound, the impinging density of the vapor beam of the antimony on said surface being such as to maintain at the carrier surface a stoichiometric excess of the antimony, the carrier temperature being about 400° to 530° C., and thereafter tempering the layer in an atmosphere of antimony vapor at a temperature close to but below the melting temperature of the indium antimonide, the antimony vapor in the tempering being at a vapor pressure lower than the vapor pressure of antimony at the tempering temperature, but higher than the vapor pressure of antimony above indium antimonide at said temperature.

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