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J. NICKL
METHOD OF PRECIPITATING CRYSTALLINE LAYERS OF
HIGHLY PURE, BRITTLE MATERIALS
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Fig.1

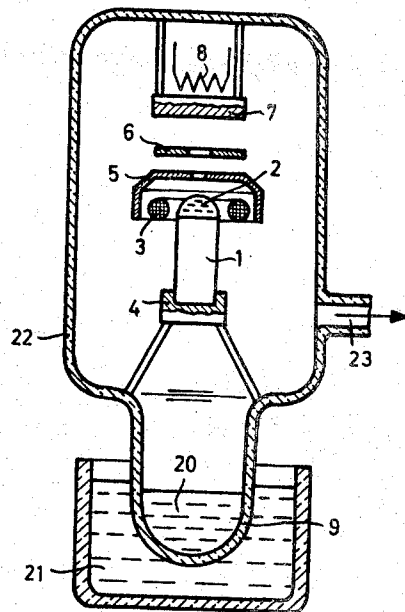
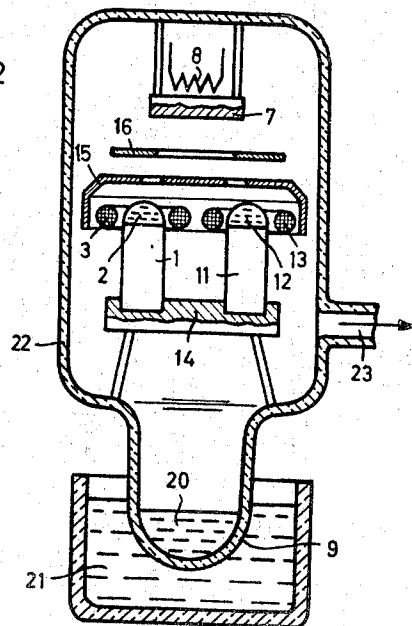


Fig.2



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METHOD OF PRECIPITATING CRYSTALLINE LAYERS OF HIGHLY PURE, BRITTLE MATERIALS

Julius Nickl, Neukeferloh, Germany, assignor to Siemens & Halske Aktiengesellschaft, Berlin and Munich, Germany, a corporation of Germany

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18 Claims. (Cl. 117—201)

My invention relates to a method of producing thin and highly pure crystalline layers of brittle materials, the term "brittle" being applied to materials which on account of a rigid crystal structure—having a lattice energy in the order of magnitude of about 200 kcal./mole—are distinguished due to a slight mobility of their atoms under normal temperature conditions. Among this group of substances, for example are silicon, germanium, carbon, boron, and $AIIBV$ semiconductor compounds such as gallium arsenide. Since atoms are only slowly built into the crystal lattice due to the slight mobility, it is difficult to obtain thin monocrystalline layers from such materials.

Although it is known to produce monocrystalline layers by precipitation from the gaseous or vaporous phase by chemical reaction, such as thermal or pyrolytic dissociation in the presence of a suitable reducing agent, it has heretofore been difficult to precipitate monocrystalline layers of the above-mentioned type of substances simply by vapor deposition, that is by vaporizing the material and causing it to condense upon a suitable carrier. Past attempts at obtaining thin layers in this manner have resulted in polycrystalline products and tend to readily scale off the supporting carrier.

It is an object of my invention to provide a method that affords the production of crystalline, brittle materials, preferably monocrystalline layers of high purity, and particularly semiconductor materials, upon a rigid crystalline carrier having the same or similar type of lattice structure, simply by the vaporization-condensation process, while avoiding the above-mentioned deficiencies heretofore encountered.

Another object of my invention is to produce by the method of simple vaporization thin semiconductor layers of the extreme purity required for electronic semiconductor purposes.

To this end, and in accordance with my invention, the material is precipitated from its vaporous phase upon a carrier in a processing vessel, and simultaneously a gaseous addition substance is supplied to the vapor in the vessel, the addition substance consisting preferably of gaseous halogens or halogen-containing compounds. These addition substances are added to the vapor in the vessel prior to or during the precipitation of material upon the carrier.

The precipitating material forms a thin layer upon the carrier which is of monocrystalline constitution and which no longer exhibits a tendency to scale off.

The layer thicknesses thus obtainable are in the order of magnitude of several powers of 10 microns, for example 0.1 to 100 microns. Vaporization of the brittle material is effected in a precipitation vessel under reduced pressure, for example by heating a rod of the material to be vaporized at one end until a melt is produced. The heating of the rod is preferably effected by means of a high-frequency induction coil.

In order to direct the vapor onto the carrier, it is of advantage to mount one or more diaphragms, preferably of molybdenum or quartz glass, between the vapor source and the carrier, so that the jet of vapor is directed through the openings of the diaphragm onto the carrier surface

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which is to be coated with a layer of the condensing material.

The temperature of the vapor source for this process is chosen so that it corresponds to a partial pressure of 1 mm. Hg at most of the material to be vapor-deposited. In other words, the vapor-deposition process is performed under relatively high negative pressure.

The partial pressures of the gaseous addition substances that are also present in the precipitation vessel are in a range of 10^{-1} to 10^{-6} mm. Hg, preferably in the range of 10^{-2} to 10^{-4} mm. Hg, and these gaseous addition substances are preferably also produced by vaporizing or boiling.

According to a preferred embodiment of the invention, a vapor pressure is maintained in the precipitation vessel at which the free path length is of an order of magnitude corresponding to the spacing between the vapor source and the carrier. In this manner the desired perfection of monocrystalline structure in the precipitated layer can be realized or more closely approached. The control or regulation of the total pressure obtaining in the precipitation vessel is preferably effected by means of a vacuum pump or simply with the aid of a cooling trap.

The production of a steep temperature gradient by cooling the vessel walls likewise has a favorable effect on the production of well-crystallized precipitation layers. A monocrystalline material of the same or similar lattice type as the one being precipitated is preferably used as carrier for the precipitating layers. However, if extreme purity is not required, an inert carrier material, preferably quartz glass, may also be employed.

During the process the carrier is heated to a temperature promoting the crystallization of the vapor-deposited material, for example to a few hundred degrees C., this temperature not being critical.

When applying the method of this invention in the production of thin layers from $AIIBV$ compounds, such as GaAs, it is advisable, although not necessary, to have halogen compounds of both constituent elements of the compound present. It rather suffices to add a halogen compound of only one of the two elements to the vaporized material. The choice of the particular halogen compound can be made on the basis of practical considerations, because it is often inconsequential as to whether a halogen compound of one or the other constituent elements is employed.

The invention will be further described with reference to preferred embodiments described hereinafter by way of example with reference to the accompanying drawings in which:

FIG. 1 shows schematically in vertical section a processing apparatus for performing the method; and

FIG. 2 shows in vertical section a modified form of such apparatus.

According to FIG. 1, a rod 1 of highly pure brittle material, such as hyperpure silicon is vertically mounted in an evacuated precipitation vessel 22 and is fastened at its lower end by means of a holder 4 which is supported by spider legs upon a shoulder portion of the vessel structure. After evacuating the vessel, the rod is heated at its upper end until a melt 2 is produced. Heat for this purpose is supplied by means of a high-frequency induction coil 3 which concentrically surrounds the upper end of the rod. The material, namely silicon, evaporating from the molten top of the rod precipitates upon a carrier plate 7 consisting also of silicon or of another material having the same or a similar lattice type. The carrier or substrate 7 is mounted at some distance above the melt. It receives the precipitating material in the form of a crystallizing layer. A heating device 8, shown to consist of an electric resistance heater, maintains the carrier 7 at a temperature

favorable for crystallization of the precipitated material, for example at a temperature of several hundred degrees centigrade, such as 200 to 900° C. Mounted between the melt 2 which constitutes the source of the silicon vapor, and the carrier 7, are two diaphragms 5 and 6 of heat-resistant material, preferably quartz glass or molybdenum. The diaphragm openings are aligned in such position that the evaporating material is directed in the shape of a limited vapor jet upon the carrier, thus preventing a vapor-deposition in the remaining processing space.

In order to provide a halogen-containing atmosphere in the precipitation vessel 22 for promotion of crystallization, the precipitation vessel is formed with a downward continuation or extension 9 which receives a suitable halogen compound 20, such as silicon tetrachloride. The extension 9 is immersed in the liquid bath 21 of a thermostat which permits heating and maintaining the liquid halogen compound at the temperature required for converting the amount of liquid into the gaseous phase needed for the required partial pressure of the halogen compound, for example 10^{-2} to 10^{-4} mm. Hg.

In order to satisfy the requirement of maintaining in the precipitation vessel a total pressure at which the free mean path corresponds substantially to the distance between vapor source 2 and carrier 7, the vessel is further provided with a suction nipple 23 for connection with a vacuum pump or cooling trap (both not illustrated).

The modified embodiment of processing equipment shown in FIG. 2 is to some extent similar to that described above with reference to FIG. 1, corresponding components being denoted by the same reference numerals respectively in both illustrations. The apparatus shown in FIG. 2 permits the production of thin layers of A^{III}B^V compounds. For this purpose, two rods 1 and 11 are vertically mounted on a holder 14, these rods consisting of the two constituent elements of the compound, for example gallium and arsenic respectively. Thin layers of A^{III}B^V compounds in addition to GaAs, such as InAs, InSb and GaSb can be similarly formed by utilizing rods 1 and 11 made of the respective constituent elements of these compounds. The liquid 20 in the extension 9 of the precipitation vessel is provided with halogen compounds of both constituent elements, or with a halogen compound of one of the two elements. The molten mounds 2 and 12 on top of the respective rods 1 and 11 can be produced by a single heating device. However, in the apparatus according to FIG. 2, two separate induction heater coils 3 and 13 are provided for this purpose. Separate openings are provided in the diaphragm 15 for the vapor emanating from each of the melts 2, 12, and an enlarged opening is provided in the diaphragm 16 to accommodate the vapor issuing from both openings in diaphragm 15. In all other respects, the equipment and the performance of the precipitation method is analogous to the embodiment described with reference to FIG. 1.

The following processing example was performed with apparatus according to FIG. 1. A silicon rod 1 having a diameter of 12 mm. and a length of 5 cm. was used. The top of the rod was heated by induction-heater coil 3 energized by alternating current of 4 megacycles per second, thus producing a self-supporting molten mound 2. At first the evolving jet of vapor was kept away from the carrier 7 by means of a lid (not shown) beneath the carrier 7. Initially, the thermostat 21 was filled with liquid air. After a period of about 1 minute, the thermostat was replaced by a vessel containing a temperature bath of -30° C. As a result, silicon tetrachloride contained in the extension 9 slowly commenced to convert to the gaseous phase. The resulting current of silicon tetrachloride gas was continuously exhausted through the nipple 23 with the aid of a mercury diffusion pump (not shown). This operation lasted about 5 minutes. Then the carrier 7, which consisted of a polished silicon disc having a diameter of 30 mm. and a thickness of 250 microns, was heated to about 800° C. by radiation from the heater 8. This temperature

was not measured during the vaporizing operation but was previously determined empirically. After a further period of 2 minutes the carrier reached the deposition temperature. Simultaneously the vapor-gas mixture in the vessel became adjusted to sustain the precipitation. Then, the above-mentioned covering lid was turned aside, thus exposing the carrier to the vapor jet issuing through the openings of the diaphragms 5 and 6, and the vapor-deposition proper began to take place. During this stage the electric power supplied to the high-frequency coil was kept constant.

After a vapor-deposition period of 10 minutes, a monocrystalline silicon layer of $2.1 \pm 0.3 \times 10^{-2}$ micron thickness was obtained.

The layers thus produced were suitable for the production of transistors, particularly mesa transistors.

When boron trichloride or phosphorus pentachloride is added to the silicon tetrachloride in the extension 9, the above-described operation results in the production of boron-doped and phosphorus-dope silicon layers.

The above-described process using equipment such as is shown in FIG. 1 can also be performed by substituting silicochloroform SiHCl₃ for the above-mentioned silicon tetrachloride, or by using analogous silicon compounds of iodine or bromine.

For vapor-depositing germanium, the liquid 20 used in the equipment according to FIG. 1 may consist of GeCl₄, GeHCl₃ or other germanium-chlorine compounds. Germanium compounds of iodine and bromine are likewise applicable.

It will be obvious to those skilled in the art, upon a study of this disclosure, that my invention can be carried out with a variety of substances and with the aid of different equipment, and consequently can be given embodiments other than particularly illustrated and described herein, without departing from the essential features of my invention and within the scope of the claims annexed hereto.

I claim:

1. The method of precipitating crystalline, particularly monocrystalline layers of highly pure semiconductor material and other brittle materials, whereby the material to be precipitated is vaporized in a reaction vessel and precipitated on a carrier of similar lattice type, located in the same vessel, which comprises directing the material to be precipitated in the form of a vapor jet upon the carrier to be coated, executing the vaporization process by maintaining the gas pressure in the precipitation vessel such that the free path length of the vapor particles lies in the order of magnitude of the distance between the vapor source and the carrier and adding gaseous halide substances of the same vaporization material whose partial pressures amount to 10^{-1} to 10^{-6} mm. Hg to the vapor of the material to be precipitated.

2. The method of claim 1 wherein the partial pressure of the halide substance added is within the range of 10^{-2} to 10^{-4} mm. Hg.

3. The precipitation method according to claim 2 wherein the substrate is monocrystalline and consists of the same semiconductor material as the one being precipitated.

4. The precipitation method according to claim 2 wherein a substrate of inert material is used.

5. The precipitation method according to claim 2 wherein a substrate of quartz is used.

6. The precipitation method according to claim 2 wherein the semiconductor material is elemental substance selected from the group consisting of silicon and germanium, and said gaseous substance consisting essentially of halogen compound of said elemental substance.

7. The method of precipitating crystalline, particularly monocrystalline, layers of pure semiconducting and other brittle materials upon crystalline carriers of similar lattice type, which comprises heating a source of the material in a precipitation vessel under negative pressure to vaporizing temperature to produce a vapor with a partial vapor pressure maximum of about 1 mm. Hg, mounting the

carrier at a cooler location of the vaporization zone in the vessel to cause precipitation of the material upon the carrier, and gasifying a halogen-containing substance to admix the resulting gas, to the vapor, at a gas partial pressure between 10^{-1} and 10^{-6} mm. Hg.

8. The vapor-deposition method according to claim 7, comprising the step of passing the evolving stream from the source to the carrier through diaphragm means of inert material to obtain a vapor jet impinging substantially only on said carrier.

9. The precipitation method according to claim 7, which comprises maintaining during precipitation the vessel space under a negative pressure at which the free path length of the vapor is in the order of magnitude corresponding to the distance between the source and the carrier.

10. The precipitation method according to claim 7, which comprises cooling the vessel walls during precipitation so as to increase the temperature gradient.

11. The precipitation method according to claim 7, which comprises heating the carrier during precipitation to elevated temperature for promoting crystallization of the precipitate.

12. The precipitation method according to claim 7, which comprises using a monocrystalline substrate of the same crystal lattice as the semiconductor material being precipitated, and precipitating a layer of 0.1 to 100 microns thickness upon the substrate.

13. The method of precipitating crystalline, particularly monocrystalline, layers of pure semiconducting and other brittle materials upon crystalline carriers of similar lattice type, which comprises heating a source of the material in a precipitation vessel under negative pressure to vaporizing temperature and directing a jet of the evolving vapor from below onto the surface of the carrier to cause precipitation of the material; and gasifying, in communication with the vessel, a halogen-containing substance at a temperature corresponding to a partial pressure of the gas lower than that of the vapor, thus admixing the gas to the vapor from which the precipitation takes place.

14. The method of precipitating crystalline, particularly monocrystalline, layers of pure semiconducting and other brittle materials upon crystalline carriers of similar lattice type, which comprises vertically mounting a rod of the material in a precipitation vessel and heating the top of the rod to melting and vaporizing temperature; directing a jet of the resulting vapor from below onto the surface of the carrier to cause precipitation of the material; and gasifying, in communication with the vessel, a halogen-containing substance at a temperature corresponding to a partial pressure of the gas lower than that of the vapor,

thus admixing the gas to the vapor from which the precipitation takes place.

15. The method of depositing crystalline layers of semiconductor material upon crystalline substrates, which comprises vertically mounting a rod of the semiconductor material downwardly spaced from the substrate surface in a precipitation vessel under negative pressure and heating the top of the rod by high-frequency induction to a vaporization temperature corresponding to a partial pressure of the evolving vapor below 1 mm. Hg, whereby material condensing from the evolving vapor precipitates upon the substrate surface; and gasifying, in communication with the vessel, a halogen-containing substance at a temperature corresponding to a partial pressure of the gas lower than that of the vapor, thus admixing the gas to the vapor from which the precipitation takes place.

16. The vapor-deposition method according to claim 15, which comprises passing the vapor from the rod top to the substrate surface through diaphragm means of inert material to obtain a vapor jet impinging substantially only on said substrate surface.

17. The method of precipitating crystalline, particularly monocrystalline layers of highly pure semiconductor material and other brittle materials, whereby the material to be precipitated is vaporized in a reaction vessel and precipitated on a carrier of similar lattice type, located in the same vessel, which comprises directing the material to be precipitated in the form of a vapor jet upon the carrier to be coated, executing the vaporization process by maintaining the gas pressure in the precipitation vessel such that the free path length of the vapor particles lies in the order of magnitude of the distance between the vapor source and the carrier and that during the production of thin layers of $A^{III}B^V$ compounds, the vapor of the precipitating material receives an addition of gaseous halide substances of a component of the vaporization material, whose partial pressures lie in the range of 10^{-1} to 10^{-6} mm. Hg.

18. The method of claim 17, wherein the partial pressure of the halide substance added is within the range of 10^{-2} to 10^{-4} mm. Hg.

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50 ALFRED L. LEAVITT, *Primary Examiner*.
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