

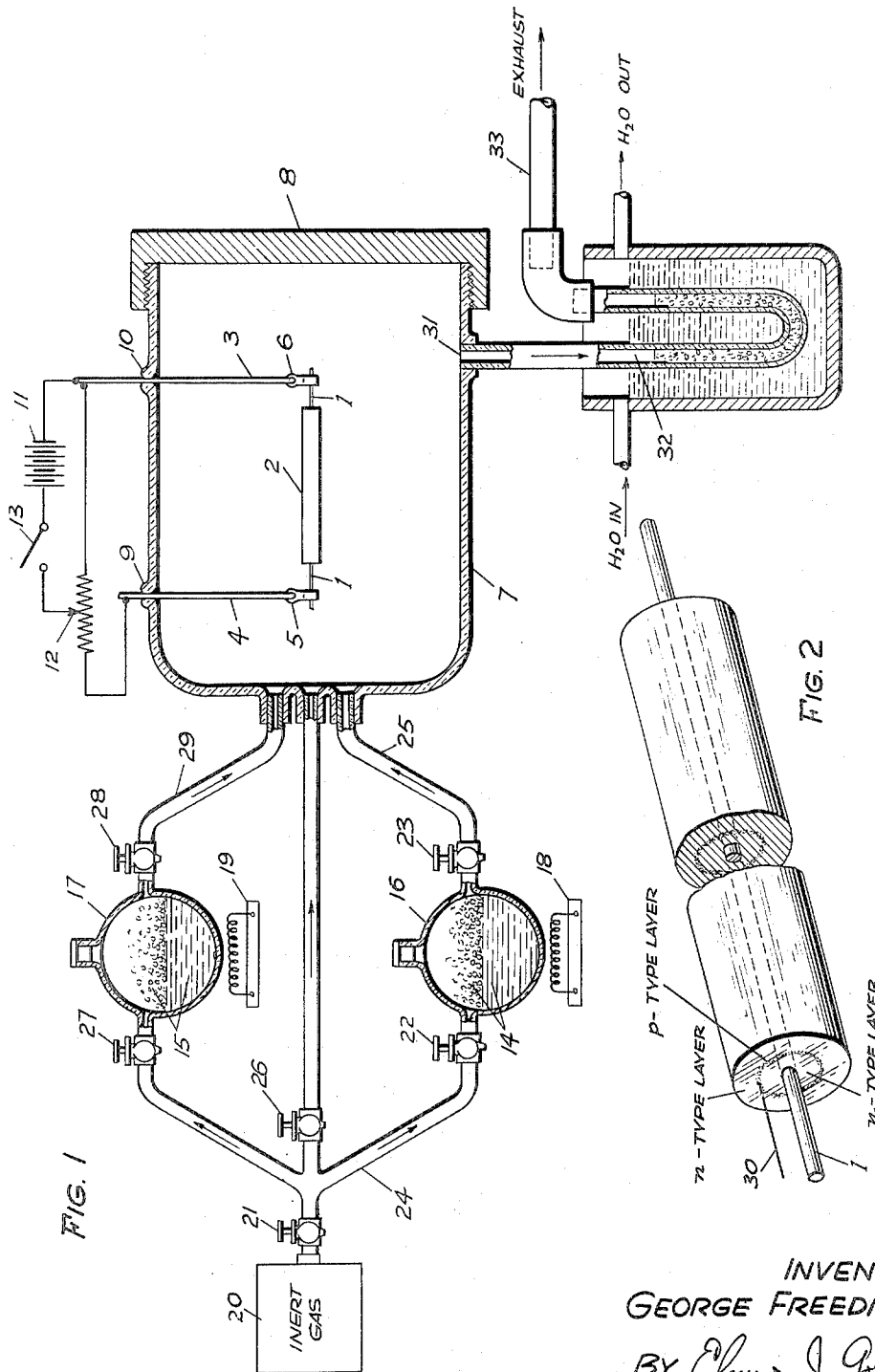
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PROCESS OF MAKING P-N JUNCTION CRYSTALS

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PROCESS OF MAKING P-N JUNCTION CRYSTALS

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This invention relates to a method of growing junction crystals and to the structure of such crystals.

In the production of transistors and diode devices, there is the problem of making single crystal alloys from semiconductor materials in a closely-controlled operation. This invention involves a novel method of making single crystal semiconductor alloys of the p-n type, p-n-p type, n-p-n type, or any combinations thereof, by alternately passing gaseous semiconductor compounds containing n- or p-type impurities over a heated member and depositing semiconductor alloys on the member. By this method, any combination of coaxial layers of n-type and p-type semiconductor alloys may be formed on the member. Such a process may be readily controlled to produce a single coaxial crystal having uniform structure and large or small n-type or p-type layers. The crystal grown may also be cut into any desired number of elements.

The invention and the above-noted and other features thereof will be understood more clearly and fully from the following detailed description with reference to the accompanying drawing in which:

Fig. 1 is a diagram illustrating apparatus which may be employed to produce semiconductor junction crystals in accordance with this invention; and

Fig. 2 is an enlarged view of a wire member on which coaxial layers of p- and n-type semiconductor alloys are deposited to form an n-p-n type junction crystal.

Referring now to the apparatus illustrated in Fig. 1, a support member 1, on which the junction crystal 2 is to be grown, is connected to insulated leads 3 and 4 by metal clamps 5 and 6. The support member 1 should be of single crystal structure, such as a single crystal tungsten or germanium wire, to act as a seed crystal on which the junction crystal 2 will grow. The support member 1 should also be of somewhat similar atomic crystalline structure to that of the semiconductor alloy to be deposited for the single crystal to grow uniformly. Therefore, when germanium alloys are being deposited, a germanium wire of single crystal structure is ideal as a support member, but a tungsten wire can be used successfully as could any wire having a crystal structure and lattice parameter which do not depart to a great degree from that of germanium, and a melting point above that of the germanium compounds to be decomposed. It should also be noted that support member 1 may also be used as an electrical connection once the crystal is deposited.

The support member 1 is suspended in a glass reaction chamber 7 having removable base 8 and seals 9 and 10 through which insulated leads 3 and 4 pass. The insulated leads 3 and 4 are connected to an electrical source 11 and to a potentiometer 12. By closing switch 13, an electrical current controlled by the potentiometer 12 is passed through the support member 1, thereby heating the support member to the proper temperature. That temperature must be maintained below the melting point of the alloy to be deposited on the support member 1, yet must be above the temperature of decomposition of the

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vaporous semiconductor compounds 14 and 15. However, the exact temperature is not critical. For example, in the case illustrated below using a tungsten wire as the support member and germanium tetrachloride as the semiconductor compound, a temperature of 900 degrees centigrade for the tungsten wire was used successfully. However, in most instances, a lower temperature is desirable in order to insure that high crystalline stability is obtained.

The semiconductor compounds 14 and 15 are contained in retorts 16 and 17, and the compounds are heated by sources 18 and 19 until they are in the vapor phase. The term "semiconductor compound" is used to denote a mixture of two compounds, one of which contains a semiconductor element, such as germanium or silicon, and the other of which contains a trace of an n-type or p-type impurity element. The n-type impurity element may be antimony, arsenic, or phosphorous, and the p-type impurity element may be gallium, aluminum, boron, or indium. For example, semiconductor compound 14 may be a mixture of germanium tetrachloride and antimony pentachloride in which germanium is the semiconductor element and the n-type impurity element is antimony. Since the boiling point of antimony pentachloride is 140 degrees centigrade, and that of germanium tetrachloride is 83 degrees centigrade, the semiconductor compound 14 should be heated to a temperature slightly above 140 degrees centigrade to place the mixture in the vapor phase. Likewise, semiconductor compound 15 may be a mixture of germanium tetrachloride and gallium trichloride in which germanium is the semiconductor element and the p-type impurity element is gallium. Retort 17 should be heated to a temperature slightly above 202 degrees centigrade (the boiling point of gallium trichloride) to vaporize semiconductor compound 15. Hydrides, rather than halides, are preferred in this operation because the hydrides generally decompose at lower temperatures where better crystalline stability is obtained.

After semiconductor compounds 14 and 15 are in the vapor phase, they are alternately pushed by an inert gas 20, for example, argon, into the reaction chamber 7 where they form the n-type and p-type layers of the junction crystal 2. This is accomplished by opening valves 21, 22, and 23 so that the inert gas 20, which is under pressure, flows through tube 24 into retort 16 where it pushes vaporous semiconductor compound 14 through tube 25 and into reaction chamber 7. There gaseous semiconductor compound 14 comes in contact with heated support member 1 and is decomposed and deposited on the support member 1 to form a coaxial crystalline layer thereon. Fig. 2 shows the support member 1 with coaxial p-type and n-type layers formed thereon. In the example described above, the n-type layer is a semiconductor alloy composed of germanium and a trace of antimony, and the p-type layer is a semiconductor alloy composed of germanium and a trace of gallium. These alloys can be changed by changing the composition of the p-type and n-type semiconductor compounds.

After depositing the first layer as desired, valves 22 and 23 are closed, and the reaction chamber 7 is flushed out with inert gas 20 by opening valve 26. After first closing valve 26, the same procedure used in regard to semiconductor compound 14 is repeated in regard to semiconductor compound 15. Valves 27 and 28 are opened and vaporous semiconductor compound 15 is pushed through valve 29 into the reaction chamber 7 so that a second coaxial layer of semiconductor alloy is deposited on top of the first layer of semiconductor alloy. As stated above, in the given example, the second layer of semiconductor alloy is composed of germanium and a trace of gallium to form a p-type layer but can be varied in composition as desired. Any undeposited semiconductor compounds are

pushed by the inert gas 20 through opening 31 in the bottom of the reaction chamber 7 and are collected in a water-cooled condensing tube 32. The inert gas 20 passes out through tube 33 and is collected in a chamber not shown.

It should be noted that, before the second layer is completely deposited, the process described above can be stopped, and an electrical conductor (see Fig. 2, Element 30) may be connected by any appropriate means to the second coaxial layer. The process may then be continued to bind the electrical conductor 30 firmly within the layer. Fig. 2 also shows a third layer labeled "n-type layer" deposited on top of an intermediate layer labeled "p-type layer." This third layer can be deposited by repeating the process described in connection with the depositing of semiconductor compound 14. Thus, an n-p-n type junction crystal can be grown, as is shown in Fig. 2. The layers in Fig. 2 may also be limited to two layers, thereby comprising an n-p type crystal. By alternating the steps described, a p-n-p type crystal, or any combination of n-type or p-type coaxial crystal layers, can be grown, as well as the n-p-n type shown in Fig. 2. The term "alternate steps," used in the specification and claims, is intended to include the various orders in which the coaxial layers may be deposited by alternating the steps in the process, as described above.

In addition to the advantages previously described, a small crystal having a very thin intermediate layer (see the p-type layer in Fig. 2) may be grown. For example, it has been determined that, if a wire support member of .0002 inch diameter is used, a crystal having a diameter of about .001 inch can be grown. Since small transistor and diode devices are often desirable, this is an important feature of this novel method of making single crystal semiconductor alloys.

This invention is not limited to the particular details of construction, materials and processes described, as many equivalents will suggest themselves to those skilled in the art. It is, accordingly, desired that the appended claims be given a broad interpretation commensurate with the scope of the invention within the art.

What is claimed is:

1. The method of making single crystal junction crystals which consists in vaporizing a p-type semiconductor compound and an n-type semiconductor compound, passing said p-type semiconductor compound in a gaseous state onto a heated single crystal member, depositing a layer of p-type semiconductor alloy on said member, passing said n-type semiconductor compound in a gaseous state onto said member, depositing a layer of n-type semiconductor alloy on said member in alternate steps to form a junction crystal, interrupting the deposition of at least one of said layers at a desired time, placing an electrical conductor in contact with said one layer, and resuming the deposition of one layer whereby said conductor is firmly embedded within said one layer.

2. The method of making single crystal junction crystals which consists in vaporizing an n-type semiconductor compound and a p-type semiconductor compound, passing said n-type semiconductor compound in a gaseous state into a chamber and onto a heated single crystal member, depositing a layer of n-type semiconductor alloy on said member, flushing said chamber with an inert gas, passing said p-type semiconductor compound in a gaseous state into said chamber and onto said member, depositing a layer of p-type semiconductor alloy on said member in alternate steps to form a junction crystal, interrupting the deposition of at least one of said layers at a desired time, placing an electrical conductor in contact with said one layer, and resuming the deposition of one layer whereby said conductor is firmly embedded within said one layer.

3. The method of making single crystal junction crystals which consists in vaporizing an n-type semiconductor compound and a p-type semiconductor compound, pass-

ing said n-type semiconductor compound in the vapor phase onto a single crystal supporting member, decomposing said n-type semiconductor compound on the surface of said member whereby a layer of n-type semiconductor alloy is deposited upon said member, passing said p-type semiconductor compound in the vapor phase onto said member, decomposing said p-type semiconductor compound on the surface of said member whereby a layer of p-type semiconductor alloy is deposited upon said member in alternate steps to form a junction crystal, interrupting the deposition of at least one of said layers at a desired time, placing an electrical conductor in contact with said one layer, and resuming the deposition of one layer whereby said conductor is firmly embedded within said one layer.

4. The method of making single crystal junction crystals which consist in vaporizing an n-type semiconductor compound comprised of an element selected from the group consisting of germanium and silicon and an impurity selected from the group consisting of arsenic, antimony, and phosphorus, vaporizing a p-type semiconductor compound comprised of an element selected from the group consisting of germanium and silicon and an impurity selected from the group consisting of gallium, aluminum, boron, and indium, passing said n-type semiconductor compound in the vapor phase onto a heated single crystal member, depositing a layer of n-type semiconductor alloy on said member, passing said p-type semiconductor compound in the vapor phase onto said member, depositing a layer of p-type semiconductor alloy on said member in alternate steps to form a junction crystal, interrupting the deposition of at least one of said layers at a desired time, placing an electrical conductor in contact with said one layer, and resuming the deposition of one layer whereby said conductor is firmly embedded within said one layer.

5. The method of making single crystal junction crystals which consists in vaporizing an n-type semiconductor compound comprised of germanium tetrachloride and antimony pentachloride, vaporizing a p-type semiconductor compound comprised of germanium tetrachloride and gallium trichloride, passing said n-type semiconductor compound in the vapor phase onto a heated single crystal member, depositing a layer of n-type semiconductor alloy comprised of germanium and antimony on said member, passing said p-type semiconductor compound in the vapor phase onto a heated member, depositing a layer of p-type semiconductor alloy comprised of germanium and gallium on said member in alternate steps to form a junction crystal, interrupting the deposition of at least one of said layers at a desired time, placing an electrical conductor in contact with said one layer, and resuming the deposition of one layer whereby said conductor is firmly embedded within said one layer.

6. The method of making single crystal junction crystals which consists in vaporizing a p-type semiconductor compound and an n-type semiconductor compound, passing said p-type semiconductor compound in a gaseous state onto a heated single crystal member, depositing a layer of p-type semiconductor alloy on said member, passing said n-type semiconductor compound in a gaseous state onto said member, depositing a layer of n-type semiconductor alloy on said member, again passing said p-type semiconductor compound in a gaseous state onto a heated member, depositing a layer of p-type semiconductor alloy on said member to form a p-n-p junction crystal, interrupting the deposition of at least one of said layers at a desired time, placing an electrical conductor in contact with said one layer, and resuming the deposition of one layer whereby said conductor is firmly embedded within said one layer.

7. The method of making single crystal junction crystals which consist in vaporizing an n-type semiconductor compound and a p-type semiconductor compound, passing said n-type semiconductor compound in a gaseous

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state onto a heated single crystal member, depositing a layer of n-type semiconductor alloy on said member, passing said p-type semiconductor compound in a gaseous state onto said member, depositing a layer of p-type semiconductor alloy on said member, again passing said n-type semiconductor compound in a gaseous state onto a heated member, depositing a layer of n-type semiconductor alloy on said member to form an n-p-n type junction crystal, interrupting the deposition of at least one of said layers at a desired time, placing an electrical conductor in contact with said one layer, and resuming the deposition of one layer whereby said conductor is firmly embedded within said one layer.

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