Nov. 24, 1964 J. J. A. ROBILLARD 3,158,511

MONOCRYSTALLINE STRUCTURE INCLUDING SEMICONDUCTORS AND SYSTEM FOR MANUFACTURE THEREOF

Original Filed March 5, 1956 2 Sheets-Sheet 1

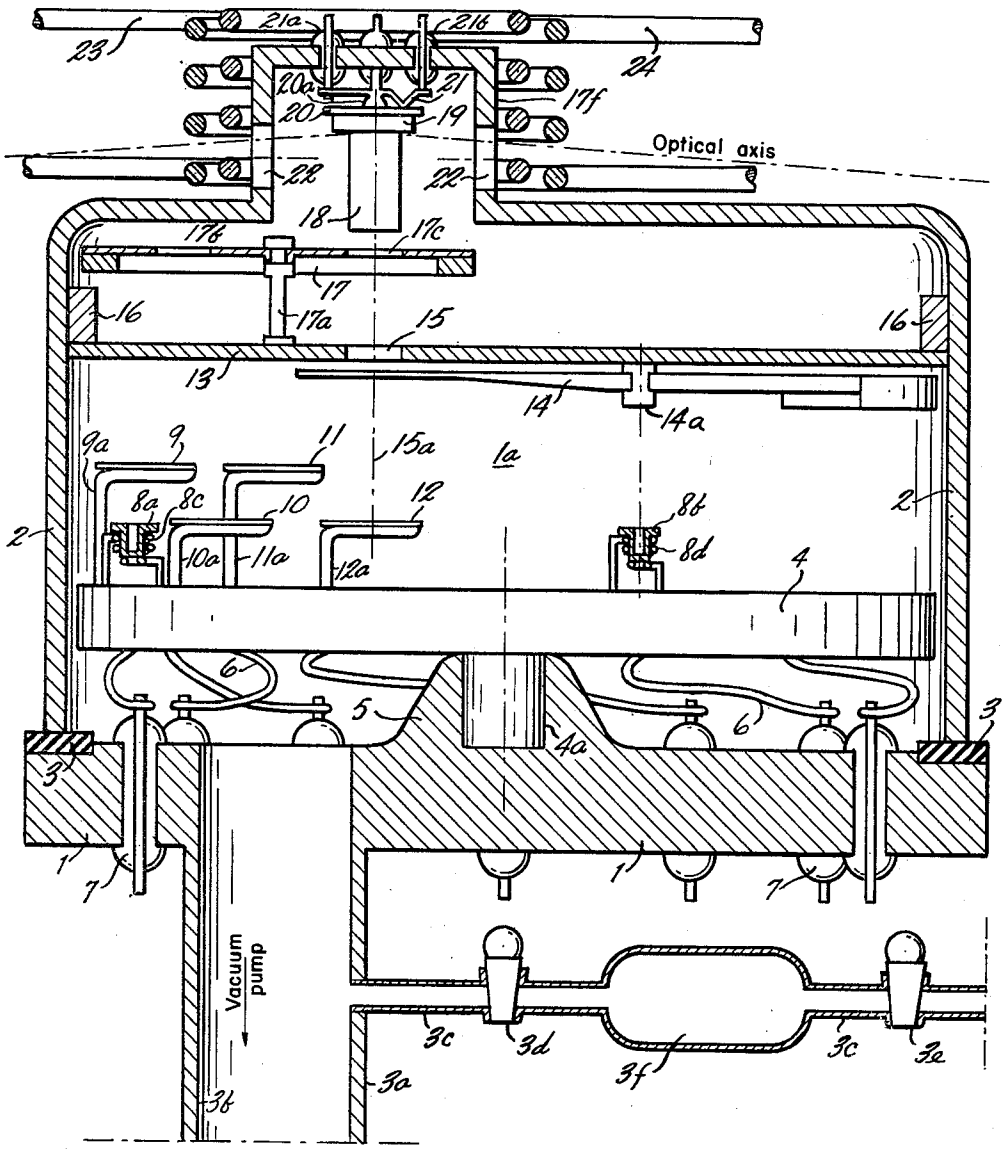


FIG. 1.

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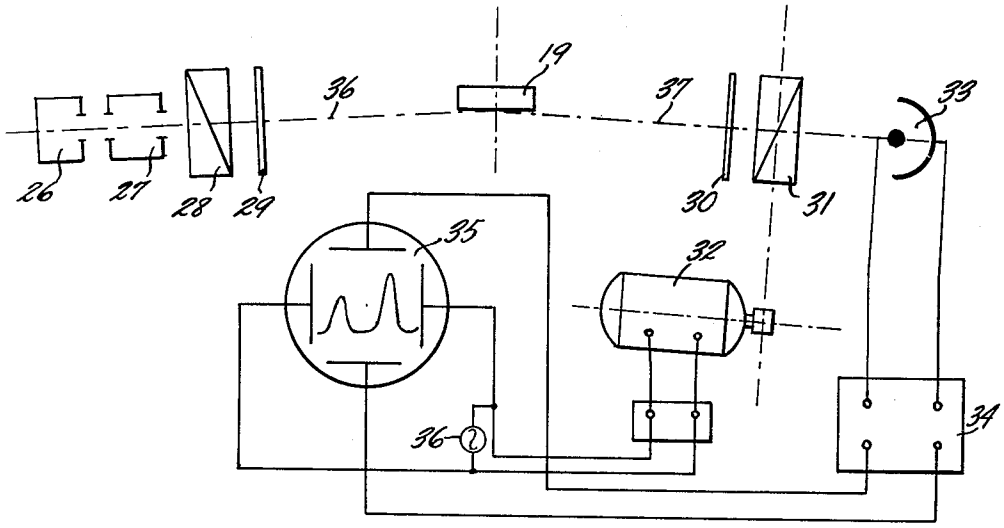


FIG. 2.

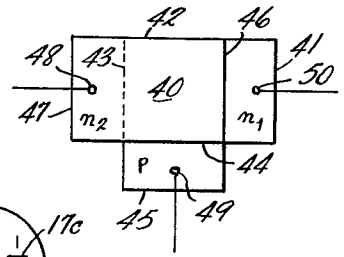


FIG. 3A.

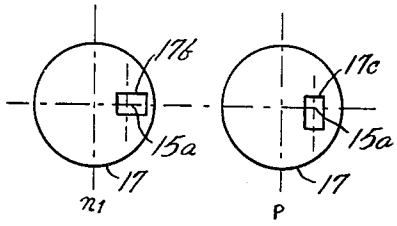


FIG. 3B.

FIG. 3C.

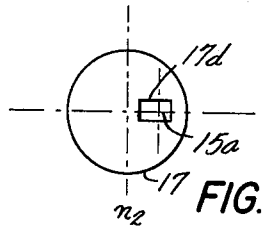


FIG. 3D.

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3,158,511

MONOCRYSTALLINE STRUCTURES INCLUDING SEMICONDUCTORS AND SYSTEM FOR MANUFACTURE THEREOF

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Continuation of application Ser. No. 569,421, Mar. 5, 1956. This application Nov. 3, 1959, Ser. No. 19,975
5 Claims. (Cl. 148—1.5)

This invention relates generally to methods and apparatuses for forming crystalline structures out of a crystallizable material. More particularly, this invention relates to methods and apparatuses of the stated sort which are adapted to form such structures from the vapor phase of the material.

The application is a continuation of application Serial No. 569,421, now abandoned, filed March 5, 1956.

An object of this invention is to form from such material a structure which is substantially monocrystalline in nature.

Another object of the invention is to maintain accurate control over the mode of crystallization of the structure during formation thereof.

Yet another object of the invention is to form a structure of the sort described which is substantially free of undesired impurities.

A further object of the invention is to provide for selective addition of small amounts of desired impurities to such structure during formation thereof.

A still further object of the invention is to form structures of the sort described of semiconductor material.

Another object of the invention is to grow semiconductor structures of the sort described in a layer-upon-layer fashion wherein different layers are of different electrical nature to permit use of the structure as, say, a transistor.

These and other objects are realized, according to the invention in one of its aspects, by providing for evaporation of the material of which the monocrystalline structure is to be made, and by further providing for condensation of the vapor of the material upon the surface of a substrate body in the form of a monocrystal having a lattice constant substantially the same as that of the monocrystalline structure to be formed. It can be shown, in this instance and under the proper environmental conditions, that the atoms of the material condensing on the substrate will be caused to be arranged in the monocrystalline form for the material. For a better understanding of this and other aspects of the invention herein, reference is made to the discussion which follows.

By way of introduction and general description, the invention herein is of application for the production of monocrystalline structures, generally. However, it is of particularly useful application when the structures produced are of semiconductor material, since thin monocrystalline semiconducting layers of germanium (Ge) of silicon (Si) prepared by evaporation of the metal under vacuum, present certain properties which make them available for purposes in the semiconductor field where the single crystal grown from a melt, according to the usual method, is not suitable.

When a metal is evaporated under vacuum its condensation on a substrate gives generally an amorphous layer or a polycrystalline layer with very small crystals. However, it has been discovered, according to the invention, that it is possible, under certain conditions, to obtain a single crystal of appreciable size.

According to the invention the crystal is grown by condensation of the metal vapor at the surface of a suitable substrate. This substrate is a single crystal which

itself crystallizes in the same system as, say, the Ge or Si crytal, and which has a lattice constant very close to the one of the crystal growing. As an example, the substrate crystal generally used for Ge is a monocrystal of sodium chloride. Furthermore, this substrate crystal is polished very carefully until a high degree of polishing (optical polishing) is reached on a plane parallel with one of the principal crystalline planes thereof, as, for example, the (100)-plane for sodium chloride. Before the condensation of the metal, this polished surface of the substrate crystal is activated by an ionic bombardment under suitable conditions of atmosphere and pressure.

During the condensation of the metal on the substrate, the temperature of the latter is kept substantially constant at a certain value which depends on the metal evaporated. This temperature is very critical and its variation should be kept to within $\frac{1}{10}$ of a degree centigrade. Every metal has its own critical temperature. Thus, for example, the value for Ge is 428° C. This condensation temperature is obtained by putting the substrate crystal in close contact with a metallic sheet (tantalum) which is heated by an external high frequency coil. This metal sheet is also in contact with a thermocouple giving an indication of the approximate temperature of the substrate crystal.

While applicant's invention is, of course, not limited by any theory propounded herein as an explanation of the phenomena which take place, it is believed that such critical temperatures exist for reasons of which some appreciation may be gained by the following simplified explanation. The atoms of the substrate crystal are in a lattice arrangement and electrically charged. As a result, there exists just above the described surface of the substrate crystal an electrical field which is periodic in both dimensions of the plane of the surface. In other words, a graphical representation of a cross-section of the field taken in a first dimension of the said plane would have the pattern of an alternating succession of maxima and minima, and a graphical representation of a cross-section of the field, taken in a second dimension of the said plane at right angles to the first dimension, would have the same pattern.

The atoms of the condensing vapor are also electrically charged, and there is an interaction between the charges of the vapor atoms and the periodic field such that the vapor atoms tend to seek positions of lowest potential energy in this field. The distribution pattern of these lowest potential energy positions is determined by and reproduces the lattice arrangement of the substrate crystal. As stated, this lattice arrangement corresponds very closely to the desired arrangement of the vapor atoms if these atoms are to define a monocrystalline structure. Hence, the vapor atoms in the course of seeking these lowest potential energy positions of the periodic field are brought by the distribution pattern of the periodic field of the substrate crystal into a mutual arrangement very close to that characterizing the true monocrystalline form of the vaporized material. Of course this initial mutual arrangement does not represent the true monocrystalline form of the vaporized material, since there is a difference between the lattice arrangement of the substrate crystal and the lattice arrangement of a monocrystal of the material. This initial mutual arrangement is, however, so close an approximation to the monocrystalline form desired that the electrical forces between the vaporized atoms themselves are sufficient to order these atoms into the mutual arrangement representing the monocrystalline form of the vaporized material.

It will be seen, however, that the capability of the vapor atoms of entering into and becoming stable in the mutual arrangement which is their monocrystalline form depends upon the component of velocity of the atoms

in the plane of the substrate surface. As is well known, this component of velocity is a function of temperature. In other words, if the temperature is too low, the velocity of the vapor atoms in the said plane will be so low that the vapor atoms will become stabilized before the atoms, in seeking the lowest potential energy positions, become sufficiently ordered, by the periodic field of the substrate that the atoms will thereafter gravitate into the monocrystalline arrangement thereof which is desired. If, on the other hand, the temperature is too high, then the vapor atoms will have such high velocities in the plane of the substrate surface that these atoms will overshoot the lowest potential energy positions and will thereafter become stabilized in positions of disorder in respect to the monocrystalline arrangement which is desired. It has been found, however, that there is a small critical temperature range at which the velocity of the vapor atoms in the plane of the substrate surface will be of proper value to allow these atoms to become positionally stabilized in the mutual arrangement which represents their monocrystalline form.

While the above explanation deals with the subject of obtaining a monocrystalline lattice arrangement of vaporized atoms deposited directly upon the substrate crystal, it will be understood that this initial monocrystalline arrangement will be perpetuated and continuously regenerated as further vaporized atoms condense upon the condensed monocrystalline surface, providing of course that the action takes place within the mentioned critical temperature range.

According to an important aspect of the invention the temperature measurement of the surface of the substrate crystal is not achieved by measuring the temperature itself but, rather, by controlling, with the help of an optical method, the growth of the single crystal. This is achieved by using the reflection of elliptically polarized light directed at low angle of incidence upon the crystal which is growing. The reflected light is analyzed by a dynamic device made of a quarterwave plate and a Nicol prism rotated by a synchronous motor. The light is finally received by a photocell which gives rise to a signal which is amplified and observed on the screen of a cathode ray oscilloscope. The time base of the oscilloscope is synchronized with the motor driving the Nicol prism. Under these circumstances the growth of a single crystal gives two maxima corresponding to the two principal directions of the ellipse for a rotation of 180°. A polycrystalline layer gives more than two maxima and, sometimes, no maximum at all (depolarization). An amorphous layer does not give any maximum. Precautions must be observed in order to avoid mistaking the reflection from the substrate for the reflection from the layer. This error can be avoided by using a very low angle of incidence.

The speed of evaporation is preferably very low in order to permit good regulation of the temperature of the substrate during all the process. Smooth control in heating the substrate can be obtained by using two high frequency heating coils with opposite fields. The substractive effects of these fields permits temperature adjustment with less thermal inertia being present than when a single coil is used. The ultimate adjustment of the temperature can also be achieved with the help of the infra-red source.

At the beginning of the evaporation the optical system gives two maxima corresponding to the reflection from the substrate single crystal. After a few minutes these two maxima tend to disappear because of the first monoatomic layers arriving at the surface. Then by varying slowly the temperature by means of one of the devices above described there will be obtained another steady state where two other maxima appear, corresponding to the growth of the new crystal. These two maxima are weak at the beginning but become more and more clear. A small variation of the tempearture on the crystal is rapidly observable by the effect thereof on the two maxima shown by the oscilloscope. It is possible to keep the right temperature by controlling the heating of the crystal holder according to the indication of the oscilloscope.

It is very important that the evaporated metal be as pure as possible. In order to obtain a good degree of purity the evaporation is preceded by a kind of molecular distillation. The metal is melted in a suitable crucible (graphite for germanium) and evaporated on a first plate of tantalum. This plate is the first one of a series of four plates placed in cascade with respect to each other. Each one of these plates can be heated by Joule-effect through electric connections at both their ends. By heating the first plate up to cause sublimation of the metal condensed on it, with the crucible being heated at the same time, part of the metal will condense on the second plate. By now heating the second plate up to cause sublimation of the metal condensed on it, the crucible and the first plate being still hot, part of the metal of the second plate will condense on the third plate, and so on, the process being continued up through the fourth plate. The metal (for example, Ge) condensed on the fourth plate has a much higher degree of purity than the metal coming from the crucible.

Another advantage of this cascade evaporation process is to be able to obtain vaporized metal from the fourth plate at a lower temperature than the temperature required for the evaporation of the metal from the crucible. The vaporized metal is obtained from a large surface and a relatively thin layer and, therefore, can be obtained by the process of sublimation. By obtaining vaporized metal in this way it is possible to accurately control the rate at which the metal condenses on the substrate, and to insure a high purity of the vapor. The rate of condensation should be kept low in order to permit a regulation of the temperature on the substrate crystal which keeps the temperture within the critical range.

The crystal obtained by this procedure may be made more suitable for use as a semiconductor in electrical applications by doping the crystal.

This doping may be achieved by evaporating an alloy, composed of the primary substance of the crystal and the doping agent, onto the surface of the crystal, and by causing a diffusion of this last-evaporated layer into the crystal by heating. A doping agent, as this term is used herein is an impurity of which a certain amount is introduced into pure germanium monocrystal to give the germanium improved semiconductive properties. The techniques of introducing such doping agents into the crystal and the various materials which are satisfactory as such doping agents are both well known to the art.

A special crucible containing the metal alloyed with the doping agent (for example, Ge with indium) is brought in front of the crystal. An evaporation is then made, the crystal being at room temperature. The condensed layer is amorphous, and the pattern given by the optical system on the oscilloscope is a random curve without any marked maximum. The quantity of doping alloy evaporated is carefully controlled by weighing the metal before the evaporation in order to get the correct percentage of dope in the crystal after evaporation and diffusion.

The diffusion of the doping layer into the crystal is achieved by heating the crystal up to a diffusion temperature which is much less than the evaporation temperature. The progress of the diffusing operation is indicated by the optical device. The end of this operation is indicated by the fact that, when the amorphous doping layer is completely diffused into the crystal, the two maxima characteristics of the crystal structure reappear on the screen of the oscilloscope.

The process above described gives a single crystal layer of semiconductor with n- or p-characteristic according to the doping agent used.

Multilayers such as, for example, (n-p), (n-p-n) or (p-n-p) can be obtained by repeating the above procedure several times and changing the doping agent. This is achieved by using several crucibles with different doping agents.

When the monocrystalline layer structure has been grown to the desired thickness, the layer is removed from the substrate crystal. This is generally done by dissolving the substrate crystal in a suitable solvent. The layer is thereafter washed and metallized on both sides in order to make contacts for the layer.

A specific embodiment of apparatus suitable for carrying out the invention is shown in the accompanying figures which are schematic only and wherein:

FIG. 1 is a side elevation of a vacuum system suitable for use in the practice of the present invention;

FIG. 2 is a diagram in side elevation of an optical and indicating system used with the vacuum system of FIG. 1; and

FIGS. 3A, 3B, 3C and 3D are diagrams explanatory of a way of obtaining a plurality of p layers or n layers or both in a monocrystalline structure formed according to the present invention.

The following description will take up in order the apparatus shown in the figures, a method for preparing a monocrystalline structure in the nature of an n-type layer of germanium, and a method for preparing a monocrystalline germanium structure characterized by N, p and n layers.

APPARATUS

Referring now to FIG. 1, the number **1** designates a base plate for a vacuum system having a vacuum chamber **1***a* hermetically sealed from the atmosphere by the base plate and by an envelope **2** which extends down over the base plate to make a vacuum-tight seal with a gasket **3** extending around the periphery of the base plate. The base plate **1** is supported by a pedestal **3***a* having a hollow interior passageway **3***b* which communicates at one end with the chamber **1***a*, and at the other end with an evacuating apparatus (not shown) which may consist, for example, of (taken in order from the vacuum chamber) a liquid air trap, a conventional mercury vapor diffusion pump, and a rotary pump. Preferably this evacuating apparatus should be able to reduce the pressure in chamber **1***a* to 10^{-7} mm. Hg. A desired amount of a gas such as water vapor may be introduced into the chamber **1***a* by a conduit **3***c* which communicates at one end with the interior passageway **3***b*, and at the other end with a source of the gas. For better control of the gas flow, the conduit **3***c* is provided with a pair of stopcocks **3***d*, **3***e* and with a reservoir chamber **3***f* located between the stopcocks.

Within the chamber **1***a*, a circular plate **4** is mounted above the base plate **1** by a pedestal **4***a* about which the plate is rotatable. The plate **4** is electrically wired to the exterior of the vacuum chamber by a plurality of electrical conductors **6** and by a plurality of bushings **7** adapted to pass electricity through the base plate to the conductors **6**. The several conductors **6** each have sufficient play in their length to permit the plate **4** to be rotated in one direction through 180°.

The rotatable plate **4** may support above its top surface a plurality of crucibles, as, say, the shown pair of crucibles **8***a* and **8***b* which are respectively encircled by the tungsten spirals **8***c* and **8***d*. Each of these spirals may be selectively energized by electricity carried through appropriate ones of conductors **6** to act as heating coils for the crucibles **8***a* and **8***b*.

The rotatable plate **4** also mounts a plurality of tantalum condensing and sublimating plates **9**, **10**, **11** and **12** each supported above the plate **4** by a pair of electrically conducting rods of which the rods **9***a*, **10***a*, **11***a* and **12***a* are shown, and of which the matching rods in each pair are in back of the rods **9***a*–**11***a* in FIG. 1. The rods in each pair thereof are respectively connected to opposite ends of the tantalum plate supported by the paired rods. Each rod is connected at its base to a conductor **6** in such manner that an electric current may be through a selected one or ones of the tantalum plates **9**–**12**. When electric current is so passed through a given tantalum plate, the ohmic resistance of the plate will cause the plate to heat up to a desired temperature as, say, 1200° C.

The purification of germanium from crucible **8***a* by the plates **9**–**12** is accomplished in the following manner. By heating crucible **8***a*, the germanium contained therein is brought to the liquid state. When in such state, there is a continuous acquisition by some of the atoms at the surface of the liquid of enough energy to overcome the forces tending to bind these atoms to the liquid, and there is, hence, a continuous escape of atoms into the vacuum above the crucible. Under the high vacuum conditions existing in chamber **1***a*, the mean free path of the escaping atoms is so long that the vaporized atoms form molecular rays which behave very much like optical rays. In this view, it will be seen that, the atoms escaping from crucible **8***a* will follow straight line trajectories, and that of all the atoms escaping from crucible **8***a*, a substantial fraction thereof will condense on the plate **9** located above the crucible.

To drive the condensed germanium atoms off the plate **9**, the plate is heated to a temperature which is below the liquefying temperature of germanium, but which is high enough to produce vaporization of germanium atoms from the condensed layer at an appreciable rate. This vaporization takes place by sublimation, i.e., by change of the germanium atoms from the solid phase (in the condensed layer) to the vapor phase, without passing through any intervening liquid phase. The advantages of sublimation are two-fold. First, the rate at which atoms vaporize by sublimation can be calculated and thus controlled much more accurately than if the atoms were vaporized from the liquid state, and this more accurate control is desirable to maintain monocrystalline rather than polycrystalline growth of the germanium condensing on the substrate. Second, the use of sublimation minimizes the undesirable phenomena, which often accompanies vaporization from the liquid state, of transportation of impurities along with the vaporized germanium atoms.

When the germanium atoms have been driven off plate **9**, the atoms travel in molecular rays in such manner that a substantial fraction of all the atoms vaporized from plate **9** condense on plate **10**. In the present instance (as discussed further under "Methods"), the crucible **8***a* is kept hot while the germanium atoms are being vaporized from plate **9**, so that the nearest cold region to plate **9** on which the germanium atoms can condense is represented by plate **10**.

The germanium atoms are advanced from plate **10** to plate **11** and from plate **11** to plate **12** in a manner analogous to that just described. Of course, while some of the germanium is lost between crucible **8***a* and plate **12**, an appreciable amount of germanium becomes condensed on plate **12** in readiness for the later vaporization therefrom (by sublimation) which directly precedes the formation of the monocrystalline layer on the substrate crystal.

The high vacuum in chamber **1***a* is advantageous in that it permits formation of the molecular rays just described. This high vacuum is also advantageous in that it frees the substrate crystal from the layer of gas which would occlude thereon under a low vacuum and which would interfere with the formation of the monocrystalline layer.

While the substance which condenses on the substrate crystal has been described as obtained by a multistage vaporization process, it is within the contemplation of the invention to condense in like manner on the substrate a substance which has gone only through a single stage of vaporization from a source such as a crucible.

Above the rotatable plate 4, the vacuum chamber 1*a* is subdivided into an upper vacuum space and a lower vacuum space by a horizontal partition member 13 of tantalum extending from one side to the other of the envelope 2. The partition member 13 is affixed to the envelope 2 by an annular ring 16 of square cross-section. An aperture 15 is formed in the partition member 13 about an axis 15*a* perpendicular to the plane of the member and shown as intersecting the plate 12.

The axis 15*a* is off center from the pedestal 4*a* which supports plate 4. Accordingly, by locating crucible 8*b* the same distance from pedestal 4*a* as axis 15*a*, and by rotating plate 4 the proper amount, the plate 12 may be moved out from under axis 15*a*, and the crucible 8*b* may be moved under this axis. Other crucibles may be moved under axis 15*a* in like manner.

The aperture 15 permits flow by molecular rays of vaporized germanium atoms from whatever source thereof happens to be under axis 15*a* to the upper part of the vacuum chamber 1*a*. This molecular ray flow may be selectively established or interrupted by a shutter 14 which is supported in hinged relation by a pedestal 14*a* downstanding from the member 13. The shutter 14 may be selectively operated by a magnet (not shown) to, in effect, close or open the aperture 15.

The partition member 13 mounts a circular diaphragm plate 17 which is supported above the partition 13 by a pedestal 17*a* about which the plate 17 is rotatable. The plate 17 has formed therein a plurality of apertures 17*b*, 17*c*, 17*d* (FIGS. 3*b*, 3*c*, 3*d*). The purpose of these apertures will be later explained.

Above the diaphragm plate 17, the envelope 2 defines a closed tubulure 17*f* which forms a well in the vacuum chamber 1*a*. Within this well a flat, tantalum, heating and support plate 20 is supported in depending relation from envelope 2 by a downstanding post 20*a*. The upper surface of the plate 20 is contacted by a thermocouple 21 which may be electrically connected up to the exterior of the vacuum chamber through a pair of bushings 21*a*, 21*b* which pass through the envelope 2. To the underside of the plate 20 there is shown attached a substrate crystal 19 upon which the monocrystalline structure of the invention is to be grown. In operation, the tantalum plate 20 is heated by passing high frequency electric current through a pair of separate coils 23, 24 encircling the tubulure 17*f*. The heated plate 20 in turn heats the substrate crystal 19.

The high frequency current for coil 23 may be obtained from a high frequency oscillator (not shown) and a first adjustable attenuator (also not shown) connected between the output of the oscillator and the coil. The high frequency current for coil 24 may be obtained from the same oscillator and from a second adjustable attenuator (not shown) connected between the output of the oscillator and coil 24. The coils 23 and 24 are so disposed in relation to each other and are so connected in polarity that the high frequency currents respectively flowing in the two coils set up electrical fields which thread the plate 20 in opposite directions. By adjusting the two attenuators, the resultant field threading the plate 20 may be accurately adjusted in magnitude to provide sensitive control over the temperature which the heated plate 20 assumes.

Beneath the substrate crystal 19 there is shown an element 18 representing an electrode for exposing crystal 19 to ionic bombardment in one stage of the method hereafter described. While FIG. 1 represents this electrode as apparently being located directly beneath crystal 19, it will be understood that this electrode is, in fact, displaced to the rear of the plane of FIG. 1 if crystal 19 is considered in the plane of FIG. 1. Another electrode 18 (not shown) is disposed opposite the shown electrode 18 to the front of the plane of FIG. 1. The two electrodes 18 are spaced sufficiently far apart that the entire polished undersurface of crystal 19 will be exposed to molecular rays passing through aperture 15. The electrodes 18 are adapted to be connected (through means not shown) to a source of high voltage, as, say, 2000 volts.

The tubulure 17*f* is provided on opposite walls thereof with a pair of windows 22, 22 of transparent material to permit light to enter and exit the tubulure so that the growth of the monocrystalline layer can be monitored by the optical system now to be described.

FIG. 2 shows the optical system used to monitor the crystalline development of the layer condensing on the substrate crystal. As shown in FIG. 2, this optical system includes a monochromatic light source 26, a collimator 27, a Nicol prism 28 and a quarter-wave plate 29 disposed in order in an optical path to project a beam of elliptically polarized light at a very low angle of incidence onto the condensed layer forming on the substrate crystal. This beam is reflected from the condensed layer along an optical path which includes, in order, a quarter-wave plate 30, a Nicol prism 31 and a photocell 33. The Nicol prism 31 is rotatable about the axis of the optical path, and is driven in rotation by a synchronous motor 32 energized by an alternating current source 36 which also synchronizes the horizontal time base generated by the cathode ray oscilloscope.

The output signal from the photocell 33 is amplified in an amplifier 34 and then is applied to the vertical deflecting plates of the cathode ray oscilloscope. Of course, the output signal from amplifier 34 may also be used to automatically control the currents in coils 23 and 24 so as to maintain the temperature of crystal 19 within the critical range.

The above-described apparatus may be utilized in conjunction with the practice of methods according to the present invention of which examples will now be described.

METHOD FOR PREPARING MONOCRYSTALLINE h-TYPE GERMANIUM

Preparation and activation of the substrate crystal.—The substrate crystal 19 is a single crystal of sodium chloride with 1.5 x 1.5 x 0.5 cm. of size, polished and transparent. This crystal is fixed into a tantalum plate 20 by putting a few drops of water at the upper surface of the crystal, and by pressing it against the surface of the tantalum plate. All the system is evacuated up to a pressure of about 10^{-7} mm. Hg. During the evacuation the tantalum plate is slightly heated to be maintained at a temperature of 100° C. by means of one or both coils 23 and 24.

After fifteen minutes the connection with the diffusion pump is closed and the vacuum chamber is kept connected with only the rotary pump. Some water pressure is introduced into the chamber through the conduit 3*c*, and the total pressure at about this time is reduced to about 10^{-1} mm. Hg and kept around this figure. At this pressure an electrical discharge of 2000 volts A.C. is produced between the electrodes 18.

The pressure is sufficiently low that water vapor particles are ionized by the electrical discharge within a fairly widespread region. As a result, the surface of the sodium chloride crystal is bombarded by ions of water vapor. Since water vapor is a solvent of sodium chloride and since the water vapor ions which bombard the crystal surface are traveling at substantial velocities, the ions will etch away the amorphous layer (i.e., Belby layer) which has been left by the optical polishing of the crystal. The etching uncovers the underlying monocrystalline structure of the sodium chloride crystal so that this substrate crystal is rendered activated to perform the function of helping bring the condensing germanium atoms into monocrystalline order in the manner heretofore described. After five minutes of the etching operation the connections with conduit 3*c* are closed, and the chamber is evacuated again up to a pressure of 10^{-7} mm. Hg. During this evacuation the substrate crystal is still maintained at a temperature of 100° C. Pumping for at least fifteen minutes is generally required before any deposition

of metal is commenced in order to eliminate all trails of water vapor.

During all these operations the shutter **14** has been kept closed.

Preparation of the metal to be evaporated.—The crucible **8***a* is gradually heated up to a temperature of 1500° C. and kept at this temperature until all germanium has been evaporated and a fraction thereof has condensed on the first tantalum plate **9**.

As the next step, the crucible **8***a* is kept at the same temperature and the plate **9** is heated gradually up to a temperature of 1200° C. until all germanium on plate **9** has evaporated, and a fraction thereof has condensed on plate **10**.

Thereafter the crucible **8***a* and the plate **9** are kept at the same temperature and the plate **10** is gradually heated up to a temperature of 1200° C. until all germanium has evaporated from plate **10** and a fraction thereof has condensed on plate **11**.

Following the last stated step, the crucible **8***a*, and the plates **9** and **10** are kept at the same temperature, and the plate **11** is gradually heated up to a temperature of 1200° C. until all germanium has evaporated from plate **11**, and a fraction thereof has condensed on plate **12**.

The germanium on plate **12** is now ready to evaporate on the substrate crystal **19**.

During all this procedure, the shutter **14** has remained closed.

Adjustment of the optical device.—As stated, the quarter-wave plate **29** is oriented with respect to the Nicol prism **28** such that its neutral lines make an angle of about 22.5° with the axis of the prism. Both prism **28** and the plate **29** are oriented in such a manner that the great axis of the ellipse is parallel to the plane of the crystal substrate. The quarter-wave plate **30** is oriented along the same principal directions as **29**. The incidence and reflection angles which the polarized beam makes with the crystal **19** are adjusted to a value of from 2 to 5°. The reflection on the substrate crystal will now give two different maxima appearing as such on the trace of the oscillograph. The device is now ready to operate.

Crystal growth.—At the beginning of the operation the shutter **14** is closed. The substrate crystal **19** is heated by means of coils **23** and **24** up to a temperature of 430° C., controlled by the thermoelement **21**.

The plate **12** is gradually heated up to a temperature of 900° C. and kept at this temperature for all of the evaporation. At 900° the germanium sublimates from plate **12** slowly enough to keep the rate of condensation of the germanium on the substrate well down within the range for which the speed of temperature response of the substrate crystal (to current adjustment in the high frequency coils) is sufficient to correct any tendency of the growing monocrystalline layer to become polycrystalline.

When the germanium begins to evaporate (observable on the lower part of the shutter **14**) and when a steady state of temperature has been reached on the substrate crystal (thermocurrent constant) the shutter **14** is opened to permit the germanium atoms to stream through the aperture **15** in molecular rays which irradiate the substrate to result in condensation of germanium atoms thereon. A few minutes after the opening of shutter **14**, the two maxima on the oscilloscope become weaker and seem to disappear. At this time by slowly changing the relative strengths of the currents in coils **23** and **24** it is possible to find a position at which the two maxima are stabilized. This state has to be kept under all the evaporation. The evaporation must be very slow in order to get a distortionless crystal.

When the evaporation has been completed, the shutter **14** is closed again, and the temperature of the substrate crystal is brought down gradually until it reaches room temperature. At that time, the two maxima can still be observed on the screen of the oscilloscope.

Evaporation of the doping layer.—In order to evaporate the doping layer, the crucible **8***b* containing the doping alloy is brought in front of the aperture **15** by rotation of the plate **4**. Then the crucible **8***b* is gradually heated with the shutter **14** closed during the outgassing period of gas from the crucible. When the evaporation of the doping agent begins, the shutter is opened and the vaporized metal condenses on the crystal surface, which is still at room temperature. During the deposition of this new layer, either the two maxima on the screen of the oscilloscope disappear again (due to depolarization) if the deposited layer is amorphous, or many other maxima appear if the deposited layer is a polycrystalline layer. When this second evaporation is completed the shutter **14** is closed again.

Diffusion of the doping layer in the crystal.—The crystal is heated up to a temperature of 350° C. by means of coils **23** and **24**. When the diffusion is achieved the two maxima observed on the screen of the oscilloscope before the evaporation of the doping layer appear again. This gives an indication that the diffusion of the doping layer into the crystal has been satisfactorily completed.

Removing the germanium crystal from the substrate.—In dissolving the sodium chloride crystal, one must be careful not to destroy the thin germanium crystal by the osmotic pressure strains arising at the interfaces between the germanium and the sodium chloride during the dissolution. In order to avoid the effect of these strains, the crystal is not dissolved in pure water, but in a solution of sodium chloride in water very close to the saturation point for sodium chloride. As the NaCl crystal is dissolved, the thin layer of germanium is caught on a thin metallic mesh and transported into pure distilled water for washing.

These thin layers give a very good contact (due to surface tension) with the metallic mesh which can be used as an electrode and which serves as a strengthener for the germanium layer.

The article which is obtained by the procedural steps just described is in the nature of a thin sheet of germanium having a monocrystalline internal structure throughout. Each of the front and back or major faces of the sheet represents a principal plane of crystallization of the monocrystal sheet. It will be noted that these major faces are activated faces in the sense that the monocrystalline structure extends right out to the face of the sheet. In this respect, the described germanium sheet differs radically from sheets of germanium which are produced by a grinding down process, and in which the grinding down action renders the material just below the face of the sheet amorphous in internal structure.

If the germanium sheet is to be used as a semiconductor, the sheet includes a small percentage of doping agent diffused thereinto in the manner already described.

The sheet of germanium may include several layers of the p-type or n-type, or both, as will later be described in further detail. A monocrystalline sheet of the sort described has many interesting properties which are not found in polycrystalline sheets, and which render the monocrystalline sheets highly useful for applications in various fields of technology. For example, the sheets may be used for interference filters in optics, or may be used in various electrical applications where the sheet is a semiconductor. It is possible by utilizing the teachings of the present invention to build up sheets of a thickness having an order of magnitude the same as that of the wavelength of visible light, or it is, on the other hand, possible to build up sheets of much greater thickness.

Electrical contacts with the crystal.—The electrical contact between the thin metallic mesh and the germanium sheet is improved by evaporation of a thin metallic layer through the holes of the mesh. Another metallic layer is also evaporated on the other side of the Ge layer in order to make the second electrode. This evaporation is made through a special diaphargm which avoids a short circuit with the other electrode. Wire connections

may now be made by means of silver paste applied to both sides of the semiconductor structure.

METHOD OF PREPARING n AND p TYPE LAYERS IN MONOCRYSTALLINE GERMANIUM STRUCTURE

The preparation of the n, p, and n layers of germanium makes use of the above-described technique three times with different doping alloys. For that purpose three different crucibles with doping alloy (two containing n-type and one containing p-type) are mounted on the base plate **4**, as well as three different germanium sources **12**. The source **12** and the alloy-containing crucibles are each arranged on plate **4** so that each of the sources and crucibles can be brought in succession and in proper order beneath the axis **15***a*.

Assume that it is desired to build up a monocrystalline body **40** having an n_1 layer above which is superposed a p layer above which is superposed an n_2 layer as shown in FIG. 3A. To build up the n_1 layer, the diaphragm **17** is rotated to bring aperture **17***b* into reference position underneath the axis **15***a* as shown in FIG. 3*b*. The n_1 layer is then formed according to the method already described, a source **12** of germanium and a crucible containing an alloy of the proper doping agent being brought in turn under the axis **15***a*.

As stated, the vaporized atoms of the germanium and of the doping agent travel in molecular rays within the vacuum chamber **1***a*, and these molecular rays have straight line paths like optical rays. As a result, the only rays which can reach substrate crystal **19** during the building up of the n_1 layer are those rays within the solid angle subtended by the aperture **17***b* and having the source of the vaporized atoms as the vertex of the solid angle. It follows that the n_1 layer will be built up on the substrate crystal only within an area which represents an approximate image of the aperture **17***b*. This area will have the outlines given by the lines **41**, **42**, **43** and **44** in FIG. 3A.

After the n_1 layer has been built up, the diaphragm **17** will be rotated to bring the aperture **17***c* (FIG. 3C) into reference position under the axis **15***a*, and the p layer will then be built up in like manner to the n_1 layer. Comparison of FIGS. 3B and 3C shows that at reference position the apertures **17***b* and **17***c* define respective areas having certain parts which are separate but having other parts which are in overlapping relation. Accordingly, the build up of the p layer in the monocrystalline body **40** will take place over an area which in part is separate from but which in part overlaps the area of the n_1 layer previously built up. This area for the p layer is outlined by the lines **42**, **43**, **45** and **46** shown in FIG. 3A.

The n_2 layer is built up in the same manner after the diaphragm **17** has been rotated to bring the aperture **17***d* (FIG. 3D) into reference position. Again, the area defined by aperture **17***d* is in part separate from but in part overlaps with each of the areas defined at reference position by apertures **17***b* and **17***c*. It follows that the n_2 layer built up in monocrystalline body **40** will likewise be separate in part but overlap in part each of the areas of the previously built up n_1 and p layers. The area of the n_2 layer is outlined by the lines **42**, **47**, **44** and **46** shown in FIG. 3A.

As shown in FIG. 3A, by constructing the monocrystalline body **40** so that the several layers thereof each have a portion which does not overlap with the other layers, it is possible to make independent connections to the several layers through the shown contacts **48**, **49** and **50**, for example.

The monocrystalline body **40** after formation thereof may be treated in the manner described under the antecedent headings "Removal of the germanium crystal from the substrate" and "Electrical contacts with the crystal." Thus the body **40** may be given a mesh backing, and a metallic layer evaporated through the holes of the mesh to form a contact electrode layer for the body **40**.

The above-described embodiments of apparatus method and article are exemplary only and it will be understood that the invention herein comprehends embodiments differing in form or detail from the above-described embodiments. For example, it is evident that evaporation and diffusion temperatures are not critical, and that, accordingly, evaporation and diffusion temperatures other than those mentioned may be utilized in the preparation of a monocrystalline germanium body. It is also evident that the invention is not limited to germanium bodies and the preparation thereof, but, also comprehends monocrystalline bodies and the preparation (apparatus and methods) of monocrystalline bodies composed of different materials than germanium as, say, silicon or other substances. Furthermore, the invention in some of its aspects is not limited to the preparation of monocrystalline bodies, but may be used for other purposes.

As another example of the scope of the invention, although the invention has been described in terms of the preparation of one monocrystalline body at a time, it is within the contemplation of the invention to prepare a plurality of monocrystalline bodies at one time.

As another example of the scope of the invention, while the methods described heretofore teach the separation of the condensed monocrystalline layer from the substrate crystal by dissolving the substrate crystal, and so on, it is within the contemplation of the invention to provide an article of manufacture comprised of the substrate crystal and of a condensed monocrystalline layer which adheres to the face of the substrate crystal and which has semiconductive electrical properties by virtue of a percentage content of an appropriate doping agent. Such article is of utility, for example, as an interference filter or to determine the intensity vs. wavelength characteristic of a body of light. Such determination may be made, in the manner taught by my copending application Serial No. 613,803, filed October 1, 1956, by creating a standing wave pattern of the various wavelengths included in the body of light, by spatially shifting the standing wave pattern relative to the layer so that different points of the pattern fall on the layer at different times in the course of the shift, and by indicating the resulting variations in the ohmic resistance of the layer.

I claim:

1. Method to observe the degree to which the monocrystalline form is exhibited by a sheet of semiconductor material as the sheet grows by vacuum deposition of said material in pure form onto a substrate monocrystal of different chemical composition than said material but having a lattice constant approximately that of said material, and as an amount of doping agent is added to said sheet by condensing an amorphous overlay of an alloy of said material and agent onto said sheet, and by heating said sheet and overlay to dissipate the latter and to concurrently diffuse said agent into the material of said sheet, said method comprising, generating a beam of monochromatic light, elliptically polarizing the light in said beam, reflecting said beam of elliptically polarized light from the surface of said sheet when said sheet is growing by condensation of said pure material, generating from light in said reflected beam a signal indicating the degree of elliptical polarization thereof as a measure of the degree to which said growing sheet is assuming monocrystalline form, thereafter reflecting said beam from the surface of said overlay when said layer and overlay are being heated as described, and generating from light in the beam reflected from said overlay surface a signal indicating the degree of elliptical polarization of the light reflected from said overlay surface as a measure of the degree to which the amorphous overlay has been dissipated by said heating.

2. Method of manufacturing a monocrystalline sheet of semiconductor material having a percentage content of a doping agent therein to improve the electrical semiconductor properties thereof, said method comprising the

steps of vaporizing an amount of a pure form of said semiconductor material into a vacuum, condensing from the vapor of said material a layer thereof onto a substrate which is a monocrystal having a different chemical composition than said material but having a lattice constant approximating the lattice constant of a crystalline form of said material, directing a beam of elliptically polarized monochromatic light onto the surface of said condensing layer to be reflected therefrom, generating from the reflected light a signal indicating the degree of elliptical polarization thereof as a measure of the degree to which said layer is assuming monocrystalline form as it condenses, heating said substrate during said condensation, adjusting said heating in accordance with said signal to maintain said substrate within the critical temperature range at which said material will condense in monocrystalline form on said substrate, thereafter vaporizing into said vacuum a substance constituted at least in part of said doping agent, condensing the vapor of said substance as an overlay on said layer, and subsequently heating said layer to produce diffusion of said doping agent into the semiconductor material of said layer to thereby produce said sheet.

3. Method of manufacturing a monocrystalline sheet of semiconductor material having a percentage content of a doping agent therein to improve the electrical semiconductor properties thereof, said method comprising the steps of vaporizing an amount of a pure form of said semiconductor material into a vacuum, condensing from the vapor of said material a layer thereof onto a substrate which is a monocrystal having a different chemical composition than said material but having a lattice constant approximating the lattice constant of a crystalline form of said material, directing a beam of elliptically polarized monochromatic light onto the surface of said condensing layer to be reflected therefrom, generating from the reflected light a signal indicating the degree of elliptical polarization thereof as a measure of the degree to which said layer is assuming monocrystalline form as it condenses, heating said substrate during said condensation, adjusting said heating in accordance with said signal to maintain said substrate within the critical temperature range at which said material will condense in monocrystalline form on said substrate, thereafter vaporizing into said vacuum a substance constituted at least in part of said doping agent, said layer meanwhile being maintained in an unheated condition, condensing the vapor of said substance as an amorphous overlay on said unheated layer, subsequently heating said layer to produce diffusion of said doping agent thereinto, producing said signal as described from said light beam during the occurrence of said diffusion, and terminating said last-named heating after said amorphous layer has disappeared as indicated by said signal.

4. A method of making a monocrystalline film by vapor deposition of crystallizable material for the film on a substrate crystal having a planar surface substantially parallel to a selected crystallographic plane of the substrate crystal, with said substrate crystal having substantially the same lattice constants as a crystalline form of the material to be deposited thereon, said method comprising placing said substrate crystal in vacuum evaporation apparatus, evaporating an amount of said material in said apparatus while heating said substrate crystal at a temperature which influences such vaporized material to condense on said planar surface of said substrate crystal, generating a beam of monochromatic light, elliptically polarizing the light in said beam, directing said beam of elliptically polarized light on to said planar surface of said substrate crystal while said vaporized material is condensing thereon to reflect such light from said surface, generating from the light in said reflected beam a signal indicating the degree of elliptical polarization thereof as a measure of the degree to which said condensing material is assuming monocrystalline form, and adjusting the heating of said substrate in accordance with said signal to maintain said substrate within a temperature range at which said material condenses in monocrystalline form on said substrate crystal.

5. A method of making a monocrystalline film by vapor deposition of crystallizable material on a substrate crystal having approximately the same lattice constants as a crystalline form of said material, said method comprising vapor depositing an amount of said crystallizable material on said substrate crystal in vacuum conditions while heating said crystal at a temperature which causes said material to condense thereon in monocrystalline form, directing a beam of elliptically polarized monochromatic light on to said crystal while said material is condensing thereon to reflect such light from the substrate crystal, generating from the reflected light a signal indicating the degree of elliptical polarization thereof as a measure of the degree to which the condensing material is monocrystalline, and adjusting the temperature of the substrate in accordance with said signal to maintain such temperature within a range in which said material will continue to condense in monocrystalline form on said substrate crystal.

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