

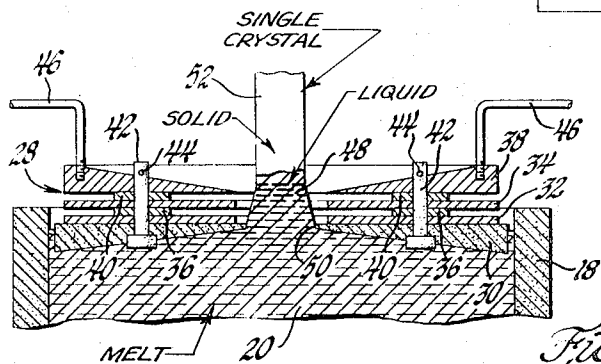
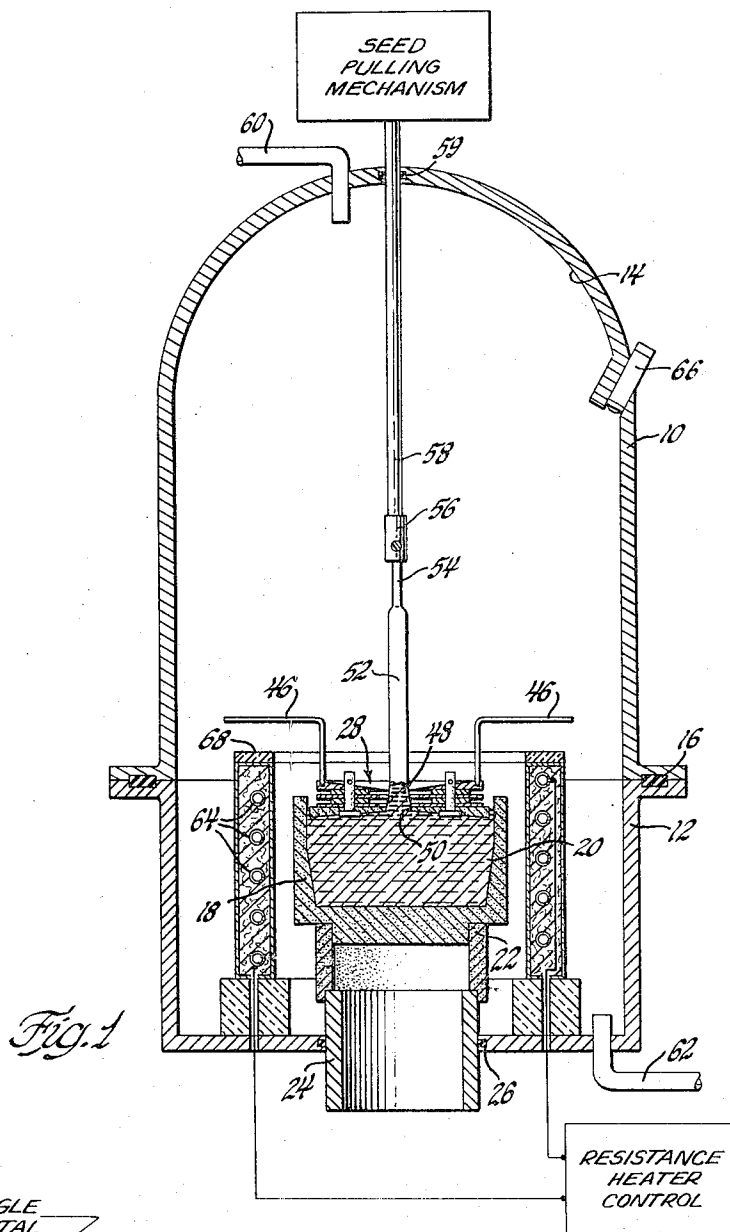
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CRYSTAL GROWTH

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1

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CRYSTAL GROWTH

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This invention relates to crystal growth and more particularly to a method and apparatus for growing monocrystalline semiconductor bodies of accurately controlled cross-sectional dimensions.

The present invention involves a process and apparatus by which one can rapidly grow a monocrystalline semiconductor rod of a very precisely controlled cross section. It permits one to grow a monocrystalline rod that need only be sliced into appropriate wafer thicknesses for use. Hence, the usual practice of trimming and dicing is avoided. Consequently, it is a much more inexpensive way of obtaining the individual semiconductor wafers used in signal translating devices, such as germanium transistors and the like. In addition, the present invention provides monocrystalline semiconductor wafers of higher quantity than that previously obtained. For example, germanium wafers exhibit no grain boundaries and have a dislocation density less than about 5,000 per square centimeter, as opposed to about 15,000 to 20,000 centimeters in conventionally obtained germanium wafers.

More particularly, the present invention involves a means for more rapidly and conveniently growing high quality, small diameter monocrystalline rods in the manner described and claimed in United States patent application 332,733, entitled "Semiconductor Crystal Growth," filed simultaneously herewith in the name of Russell M. Pierson, and which is incorporated herein by reference.

It is therefore a principal object of the present invention to provide an improved method and apparatus for the production of high quality, small diameter monocrystalline semiconductor bodies of accurately controlled cross-sectional dimensions.

Other objects, features and advantages of the invention will become more apparent from the following description of preferred examples thereof and from the drawing, in which:

FIGURE 1 shows a schematic sectional view of an apparatus for growing crystals in accordance with the invention; and

FIGURE 2 shows an enlarged schematic fragmentary view of the crucible cover assembly shown in FIGURE 1.

Monocrystals are grown by forcing a domical projection of a melt for growing monocrystalline bodies through an aperture, contacting the domical projection with a seed crystal and pulling a single crystal from the domical projection while simultaneously regulating the contact area between the single crystal and the domical projection. Hence, the single crystal is drawn from the upstanding domical projection of the melt rather than from the entirety of the melt. The melt projection is formed through an aperture in a weighted composite melt cover assembly. The assembly includes an annular weight, heat-reflecting elements and support means to effect contact between the melt and the cover assembly as desired.

The contact area between the solid single crystal and the melt domical projection is regulated to accurately control the cross-sectional dimension of the single crystal being grown. The distance between the solid-liquid interface and the cover surface, melt projection zone length, is monitored and regulated to control the size of the crystal grown.

2

The invention can more easily be described by reference to the drawing. FIGURE 1 shows a generally cylindrical, closed stainless steel furnace having an upper part 10 and a lower part 12 defining a closed furnace chamber 14. An annular silicone rubber seal 16 is used to seal the mating flanged ends of furnace parts 10 and 12. A graphite crucible 18 containing a germanium melt 20 is supported on a closed fitting graphite tube 22 which, in turn, rests on a close fitting stainless steel tube 24 which is movable through the base of lower furnace part 12. An annular silicone rubber seal 26 in the base of furnace part 12 surrounds the outer periphery of tube 24. A graphite melt cover assembly 28 is disposed on the surface of the germanium melt 20 within the crucible 18.

As can be seen more clearly in FIGURE 2, the cover assembly 28 includes a graphite cover element 30 resting directly on the surface of the melt 26. A 0.008 inch thick molybdenum ring 32 rests directly on the upper surface of the cover element 30. Another 0.008 inch thick molybdenum ring 34 is disposed above molybdenum ring 32 and spaced therefrom by means of molybdenum spacing elements 36 of similar thickness. An annular stainless steel or molybdenum weight 38 lies in spaced relationship above molybdenum ring 34, spacing being achieved by means of 0.008 inch thick molybdenum spacing elements 40. Graphite bolts 42 extend through the cover member 30, molybdenum rings 32 and 34 and the stainless steel weight 38. Stainless steel retaining pins 44 extend through bolts 42 above weight 38 to lock the cover elements together as a composite assembly. Side arm crucible cover assembly support elements 46 are threaded to the annular weight 38. The combined weight of the cover assembly 28 induces a projection 48 of the germanium melt 26 up through a central aperture 50 in the crucible cover element 30. The central apertures in each of the molybdenum rings and the annular weight are somewhat larger than the cover aperture 50 to avoid contact with the melt projection.

As can be seen in FIGURE 1, a solid monocrystal 52 grown from the melt depends from a seed crystal 54 and is in contact with the melt projection 48. The seed crystal 54 is supported by a chuck 56 which is connected to an appropriate pulling mechanism for growing monocrystals via shaft 58. The upper furnace part 10 has a central opening therein through which seed-pulling shaft 58 extends. An annular silicone seal 59 is used to seal the aperture surrounding shaft 58. Tubes 60 and 62 are used to provide the desired protective atmosphere within the furnace chamber 14. Gases, such as nitrogen, hydrogen, argon, helium or the like, can be used as furnace atmospheres. The melt 26 in crucible 18 is heated by means of a resistance heater 64 surrounding the crucible. Suitable temperature sensors (not shown) are appropriately located to precisely measure melt temperature. Exterior radio frequency induction heating can also be used along with appropriate furnace modifications in the known and accepted manner.

A small telescope 66 is appropriately located in the upper furnace part 10 to monitor the melt crystal interfacial area during crystal growth. A graduated scale within the telescope is calibrated for accurate measurements of the distance between the melt crystal interface and the upper surface of the cover for accurate control of the crystal diameter. In actual dimension the crucible cover rings 32 and 34 are sufficiently thin as to allow easy viewing of this interfacial area. The upper surface of weight 38 is inwardly tapered to facilitate this viewing. When the stainless steel tube 24 is lowered, the side arm supports 46 of the crucible cover assembly come to rest on the upper end 68 of the resistance heater 64.

In this manner the cover assembly 28 is supported out of contact with the melt 20. After the crucible 18 is charged with the melt and the melt fused, the tube 24 can be raised to position the cover assembly 28 on the fused melt as shown in the drawing.

In order to grow a monocrystalline germanium rod of accurately controlled cross-sectional dimension in accordance with the invention, the furnace part 10 is raised, cover assembly 28 lifted and crucible 18 appropriately charged with germanium prepared in the normal and accepted manner. For example, 40 ohm-centimeter germanium ingot is etched in an equimolar mixture of nitric acid, acetic acid and hydrofluoric acid. It is then rinsed with deionized water, rinsed with methanol and dried. The germanium ingot is then placed in the crucible, along with sufficient impurity to suitably dope the melt, if concurrent doping is desired. An impurity content on the order of approximately 1 part per million is frequently employed. The cover assembly 28 is rested on the heater end 68 and the upper furnace part 10 lowered into engagement with lower furnace part 12 to form a closed furnace chamber.

The furnace is then purged. The usual furnace gases for crystal growing can be employed including inert gases, nitrogen-hydrogen mixtures, substantially pure hydrogen or the like. In some instances it may be desired to use a vacuum. The crucible 18 is preferably positioned low enough in the heater 64 to allow fusion of the melt before the cover assembly 28 is floated on the melt. The charge is then melted. After the fusion of the melt, the crucible 18 is raised to float the cover assembly 28 on the surface of the melt, as shown in the drawing. The melt is initially held at a temperature somewhat above the usual growing temperature. If appropriately weighted, the crucible cover assembly 28 will be supported by the melt 20 forcing a domical projection 48 of the melt up through the cover aperture 50.

For a one and one-half degree inwardly tapered crucible having a maximum inner diameter at its mouth of approximately 2.156 inches, a crucible cover having an outer diameter of approximately 2.152 inches and a 0.4 inch circular central aperture can be used. The lower surface of the cover member is inwardly tapered at about six degrees to an edge thickness of approximately 0.01 inch around the central aperture, forming a generally convex, or frusto-conical surface on the underside of the cover. A combined cover assembly weight comprising about 4-6 times the weight of germanium displaced, e.g., about 50 grams, is generally preferred.

A seed crystal having a 1,1,1 plane parallel to the surface of the melt is brought into close proximity of the domical projection for preheating. The melt temperature is retained at 5° C.-10° C. above its melting point. After preheating approximately five minutes, the seed is lowered into the domical projection for a slight melt-back. The temperature is then dropped in small increments until precipitation of the melt commences on the seed crystal. The pull mechanism is then initiated to slowly withdraw the seed crystal from the melt as the crystal grows without breaking contact between the solid monocrystalline body and the melt projection. If desired, the speed of the pull mechanism is then increased slightly to reduce the contact area between the domical projection and the single crystal to initially reduce crystal diameter as much as is practical before growth at the desired diameter to improve crystal quality. The speed of pull is then gradually increased, along with appropriate temperature adjustments until the desired rate of pull has been obtained. Temperature is continually adjusted, gradually dropped, as the speed of pull is increased.

The projection should be in the center of the heat field or the crystal will not grow symmetrically. Hence, during these preliminary steps, the heat field is adjusted to center it on the projection 48. If not, an elliptical crystal may result. A similar result is attained if the direc-

tion in which the crystal is pulled is not substantially vertical.

When the appropriate melt-crystal interfacial diameter is attained at the desired speed of pull, the temperature and speed of pull are held constant for substantially the balance of crystal growth. Interfacial diameter is measured by measuring the same length between the melt-crystal interface and the upper surface of cover element 30. Appropriate adjustment of temperature is thereafter made to attain the desired zone length; hence, crystal diameter. When this condition has been substantially stabilized, both temperature and speed of pull are held constant for substantially the balance of crystal growth. To terminate crystal growth, the speed of pull can be increased to break contact between the crystal and the domical projection. Once this contact is broken, crystal withdrawal is terminated so as to avoid rapid quench of the freshly grown end portion of the crystal. Subsequently, the crucible is lowered to rest the cover assembly support arms 46 on the upper edge 68 of the heater 64 and break contact between the melt and the cover assembly. The furnace is then shut down in the normal and established procedure for furnace shutdown in germanium crystal growth.

By removing the cover assembly 28 from the melt prior to solidification of the melt, the cover assembly can be reused. If not removed, expansion of the solidifying germanium through the cover aperture 50 will fracture cover member 30. Thus, the invention not only provides means to facilitate floating the cover on the melt but also means to facilitate removing the cover from the melt to permit reuse of the cover.

High quality crystals of about 0.358 inch, plus or minus 0.005 inch, can be consistently grown in this manner at rates up to 15 inches per hour. For the faster rates of growth, it is preferred to grow at a constant temperature and final regulation of diameter control effected by slight changes in pull speed, just the opposite from that described in the preceding example. Thus, either or both diameter control techniques can be used to arrive at the constant speed-constant temperature condition that produces constant diameter in the crystal being grown.

The molybdenum rings 32 and 34, as well as weight 38, serve as heat reflectors to reduce heat loss from the top of the melt. Hence, lower growing temperatures can be used to obtain faster rates of growth. The spacers 36 and 40 are used to minimize direct heat transfer by conduction from one cover assembly element to another. In addition, the annular weight stabilizes the cover assembly, provides more uniform weight distribution and facilitates handling of the cover assembly as a unit.

The diameter of the crystal which is being grown will vary by changing the area of contact between the crystal and the domical projection. I have found that changes in the zone, particularly its length, between the surface of the cover element 30 and the melt-crystal interface, accurately reflects size changes in interfacial area. Consequently, zone length can be monitored and regulated during crystal growth to accurately control diameter of the crystal being grown. Since the liquid projection differs significantly in color and brightness from the graphite surface and the solid crystal, the annulus formed by the surface of the projection can be accurately located and measured. However, monitoring the change in the angle of the zone with respect to the cover surface, or the crystal pull axis, can also be used, as is described in United States patent application 332,708, entitled "Control of Crystal Size," filed simultaneously herewith in the names of Hubert G. Dohmen and Herbert A. Sims.

The aperture in the crucible cover need not be circular if a mono-crystalline rod of generally square cross section is desired. Best crystal conformity is attained by using a small zone length with other than circular cover apertures to minimize surface tension effects. In this

5

manner the rods having polygonal cross sections can be grown.

Analogously, the crucible configuration can vary to some extent. As shown in FIGURE 1, the crucible may have no taper at all in the upper area where the cover assembly is located on the melt surface. On the other hand, the crucible may have a slight inward taper from top to bottom. Of course, in such a crucible, the cover should have a sufficiently small diameter to allow the cover to drop into the crucible to a sufficient depth. The space between the outer periphery of the cover and the inner periphery of the top of the crucible can be varied without objectionable results. Since germanium surface tension forces tend to stabilize the cover within the crucible, the melt projection maintains its position very well. Of course, the inward taper on the crucible is desired for crucible protection during freezeout of the melt when growth has been terminated.

The height of the domical projection 48 is increased in a plurality of ways. The lower surface of the cover member is of a generally concave or frusto-conical configuration. Hence, the cover edge adjacent the aperture is extremely thin. Moreover, if the lower corner of this thin edge is rounded, additional projection height can be increased so that the projection extends substantially from the upper surface of the cover, not the lower surface. However, of greatest importance in forming the projection is the impression of a force on the germanium to push a domical projection through the aperture to useful height. As described, this force is applied by the combined weight of the cover assembly. Since the surface tension forces of germanium are extremely strong, much more weight can be placed on the cover than one might ordinarily expect. I prefer to employ weights equal to about 4-6 times the weight of germanium displaced by the cover. In general, an empirical formula which can be used to approximate the weight to be employed for any given crucible-cover assembly combination is determined by the following formulae:

$$(I) \quad P' = 4t/r$$

where

t = surface tension and

r = radius of the cover aperture.

(II) P'' = weight of cover assembly/area of cover surface in contact with germanium.

P' should be larger than P'' . As a safety factor, P'' of Equation II is generally held to be approximately two-thirds of P' . For greater accuracy, the buoyancy effect of the germanium displaced can also be included in P' . However, it is preferred to experimentally optimize the weight used to obtain the safest maximum projection height for any crucible-melt cover combination used.

Other modifications of the invention will be obvious to those skilled in the art and, for this reason, it is understood that the preceding description is intended only to serve as an illustration of the main features of the invention. There is no intention to be limited thereby except as defined in the appended claims.

I claim:

1. An apparatus for growing a monocrystalline body of controlled cross section, said apparatus comprising means for containing a crystal growing melt in a crystal

6

growing environment, a melt cover member having an aperture therein for contacting the surface of said melt, said member being substantially inert to its environment, means for forcing a domical projection of said melt up through said aperture above the upper surface of said cover, means for pulling a single crystal from said melt domical projection by progressive uniaxial solidification of said melt on a seed crystal above said cover member, and means on said cover for inhibiting radiation of heat from the outer surface of said cover member to the crystal growing environment above the domical projection.

2. The apparatus as described in claim 1 in which the means for inhibiting radiation of heat from the cover member to the crystal growing environment above the domical projection is an assembly comprising a first heat reflecting element adjacent the cover surface and a second heat reflecting element spaced from the first element in which the first element reflects radiant heat back to the cover and the second element reflects radiant heat back to the first element.

3. The apparatus as described in claim 1 in which the means for inhibiting radiation of heat from the cover member to the crystal growing environment above the domical projection is an assembly comprising a first annular, disk-like, heat reflecting element over said cover member substantially corresponding to and closely adjacent the outer surface of said cover member, a second annular, disk-like, heat reflecting element substantially corresponding to and closely spaced above the first heat reflecting element, an annular cover weight tapered toward its lower inner periphery closely spaced above the second heat reflecting element, and means for mutually closely spacing said elements and weight one above the other and for transmitting the force of the cover weight to the cover.

4. The apparatus as described in claim 3 wherein the assembly also includes the melt cover member, means for securing the elements and weight to the cover, and means for lifting the assembly, including the cover, from the surface of the melt.

5. The apparatus as described in claim 4 wherein the heat reflecting elements are of molybdenum.

References Cited by the Examiner

UNITED STATES PATENTS

1,450,464	4/1923	Thompson	148—1.6
2,809,136	10/1957	Mortimer	23—301
2,839,436	6/1958	Cornelison	148—1.6
2,893,847	7/1959	Schweickert et al.	23—273
2,927,008	3/1960	Shockley	148—1.6
2,944,875	7/1960	Leverton	23—273
2,956,863	10/1960	Goorissen	148—1.6
3,002,824	10/1961	Francois	148—1.6
3,025,191	3/1962	Leverton	148—1.6
3,031,403	4/1962	Bennet	148—1.6
3,096,158	7/1963	Gaule et al.	23—301
3,124,489	3/1964	Vogel et al.	148—1.6

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