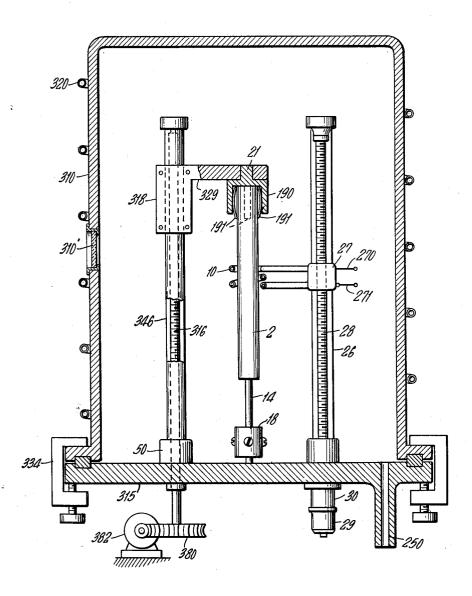
METHOD FOR PRODUCING SEMICONDUCTOR CRYSTALS Filed Feb. 18, 1959



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3,159,459 METHOD FOR PRODUCING SEMICONDUCTOR CRYSTALS

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Filed Feb. 18, 1959, Ser. No. 794,075
Claims priority, application Germany, Feb. 19, 1958,
S 57,004
3 Claims. (Cl. 23—301)

My invention relates to a method for producing semiconductor crystals for use in rectifiers, transistors, photodiodes and other electrical semiconductor devices.

The main component of such devices is an essentially monocrystalline wafer of the particular semiconductor material, for example germanium, silicon, or intermetallic compounds of elements from the third and fifth groups of the periodic system, such as indium antimonide, indium arsenide or gallium phosphide. As a rule, the monocrystals are produced by a crystal pulling method. One way of performing the method is to mount a monocrystalline seed on the end of a polycrystalline rod and to thereafter melt the rod in a narrow zone which is caused to travel from the seeded end to the other end of the rod. Such zone melting is preferably carried out without the use of a crucible. The progressing method zone, upon resolidification possesses monocrystalline constitution. The semiconductor rod, thus converted into a monocrystal, is subsequently sliced into a number of wafers to be used for the manufacture of the above-mentioned electric semiconductor devices.

For most technological applications of semiconductor devices, the life time ( $\tau_{\rm eff}$ ) of the minority charge carriers in the semiconductor material is of decisive importance. It has been observed that many zone-melted products exhibit relatively low values of  $\tau_{\rm eff}$ , particularly

at the seed end of the rod.

It is therefore an object of my invention to eliminate this deficiency and to devise a method capable of affording a better quality of the pulled or zone-melted monocrystals.

According to the invention, the method for converting a polycrystalline semiconductor rod by crucible-free zone melting into a monocrystal with the aid of a crystal seed fused to one end of the rod, is carried out by fusing to the rod a crystal seed whose cross section, especially at this fusion junction is considerably smaller than that of a semiconductor rod. Preferably, the cross section of the seed crystal is made at least one order of magnitude smaller than the cross section of the semiconductor rod, that is, the cross section of the seed is preferably smaller than about one tenth of that of the rod. When starting the zone melting operation, it is preferable, as in the known methods, to first melt the original fusion zone between the seed and the polycrystalline rod and then cause the molten zone to travel away from that location toward the other end of the rod.

The invention is predicated upon the following consideration. The temperature gradient dT/dL, in which L denotes the length of the rod, in the rod portion adjacent to the crystal seed increases with an increase in cross section of the seed. This is the case because, with a large seed cross section, a correspondingly great amount of heat is dissipated to the holder means to which the seed is attached. However, such great temperature gradient produces thermal tensions in the monocrystals and hence causes lattice disturbances which, in turn, result in reducing the life time of the minority charge carriers.

In addition, impurities in the crystal seed diffuse through the fusion junction into the semiconductor rod. Consequently, the quantities of impurities that can enter into the rod from a seed of given impurity concentration in2

creases with the cross section of the fusion junction and hence with the cross section of the seed crystal.

It is also probable that lattice dislocations present in the crystal seed may be transferred to, and increase in, the rod. Therefore, crystal seeds of a given density of dislocations will transfer more dislocations into the rod the larger the diameter of the respective seeds.

The considerations which led to the invention have been confirmed by tests, in actual practice. By using crystal seeds of considerably smaller diameter than the rod diameter, a considerable improvement in quality of the pulled or zone-melted monocrystal has been obtained. There resulted an increase in the life time  $\tau_{\rm eff}$  of the minority carriers, a stabilization of high  $\tau_{\rm eff}$  values, and a considerable reduction of the etch pit densities at the rod ends to which the crystal seed was fused. Since the occurrence of the so-called etch pits permits a conclusion to be drawn in respect to the presence of lattice faults, the observed reduction in density of the etch pits is believed to be convincing evidence for the correctness of the above-mentioned considerations.

The method can be used analogously when pulling monocrystals from a melt in a crucible.

This invention is primarily an improvement in the crucible-free floating zone processes described in the copending applications of Reimer Emeis, Serial No. 727,610, filed April 10, 1958, and Serial No. 409,610, filed February 11, 1954, assigned to the same assignee.

A specific embodiment of the process will be described in connection with the accompanying drawing, which is in vertical section.

The semiconductor rod 2, of silicon, or germanium, is fused at its lower end to a coaxial stub or seed crystal 14, of monocrystalline silicon, or germanium, respectively. The cross-sectional areas of the contact, i.e., the fusion or boundary regions of the rod 2 and seed crystal 14 are in the ratio described above. The rod 2 may have a diameter of 18 mm., and the seed crystal may have a diameter of 5-6 mm. A high frequency current is supplied, at terminals 270, 271 to the longitudinally movable induction coil 10. The coil is spaced from and is moved along the rod 2, and also along seed crystal stub 14, by a motor 29 through transmission gear 30, which gear turns spindle 28. Coil 10 is mounted upon an internally threaded slide block 27. The slide block is guided by upright bar 26. At 191 are strips of molybdenum, which serve as an auxiliary heater in the manner described and claimed in application Serial No. 727,610 of R. Emeis, mentioned above. The spring strips 191 are held between upper holder 190 and the semiconductor rod 2. Holder 190 is supported by bracket 329 carried by internally threaded slider 318. At 50 and 346 are support means for the spindle. The spindle 316 is turned by motor 382 through gear 380. The molten zone is thus caused to move upwardly from the seeded location. The molten zone is preferably limited to a length and volume such that surface tension effects are sufficient to support the molten material, as revealed in the above-mentioned Emeis applications. Said molten zone is known to the art as a floating zone. The upper end of the rod 2 may thereby be pulled upwardly, during the zone melting and monocrystal pulling operations. This is also described in said copending application of R. Emeis. Gear and motor means (not shown) can be employed to turn either or both of the holders 191 and 18, as described in said Emeis application.

A steel dome 310 encloses the apparatus. The dome is cooled by water coil 320, and is provided with an observation window 310' of refractory glass, also as described in Emeis application Serial No. 727,610. A pumping device (not shown) is attached to pipe 250 to maintain high vacuum in the device. The dome is clamped at 334 to

bottom plate 350.

I claim:

1. In a method of producing a semiconductor single crystal by processing an elongated piece of semiconductor meltable material by crucible-free floating zone melting, the method comprising seeding a location on said material with a monocrystal of said material, and comprising supporting the material in a vertical position, and heating a cross-sectional zone of said material to a temperature high enough to liquefy said material, the molten zone being sufficiently small so that the surface tension of the molten 10 material retains it in said zone, and including displacing said zone-heating longitudinally with respect to said material to said location, the improvement in said method comprising employing as said monocrystal one whose area of contact with the piece of material is not greater than 15 one tenth of the cross-sectional area of the latter.

2. The method of producing a semiconductor single crystal of silicon material by crucible-free zone melting, which comprises supporting an elongated piece of silicon vertically from above, fusing an end portion of a silicon 20 monocrystal to the lower end of said piece, supporting the opposite lower end portion of the seed crystal, inductively heating a cross-sectional zone of said piece to liquefy the material by subjecting it to a high-frequency electric field of limited longitudinal extent, the molten zone being sufficiently small so that the surface tension of the molten material retains it in said zone, displacing said zone-heating longitudinally with respect to said piece, said displacement including displacement upwardly from the monocrystal, said monocrystal having an area of contact with the piece 30 of material not greater than one tenth of the cross-sectional area of the latter, whereby heat conduction from the monocrystal through the adjacent support location is diminished and transfer of faults from the monocrystal to the piece of silicon is diminished.

3. The method of producing a semiconductor single

crystal by crucible-free floating zone melting, which comprises supporting an elongated piece of semiconductor material vertically from above, fusing an end portion of a monocrystal seed crystal to the lower part of the piece, supporting the opposite lower end portion of the seed crystal, heating a cross-sectional zone of said piece to melt the same, the molten zone being sufficiently small so that the surface tension of the molten material is sufficient to retain it in said zone, displacing said heating lengthwise of the piece, said displacement including displacement from the seed, said seed having an area of contact with the piece of material not more than about one-tenth of the cross-sectional area of the piece at the region of con-

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