R.K.

LB-892

PREPARATION OF SINGLE CRYSTALS OF GERMANIUM AND SILICON

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Introduction

This bulletin describes a laboratory technique of preparing single crystals of germanium and silicon utilizing a compact, dependable furnace. In this method, a properly oriented single-crystal seed is touched to the surface of the molten metal, which is held close to its melting point. The seed is then slowly raised, and the liquid, which is withdrawn, is converted into a single-crystal rod. The apparatus is simple and easily applied to germanium; silicon is more difficult to prepare but has also been successfully grown in the same apparatus. Crystals ranging from 1/8 inch to 1½ inches in diameter and up to 18 inches long have been made.

General Considerations

Because of the recombination and concomitant annihilation of holes and electrons at grain boundaries, it is essential that germanium rectifier and transistor material be single crystalline. The crystal must further be free of other imperfections such as twin bands, lineage, dendritic structure and deformations in general, which are expected to affect adversely such properties as carrier mobility, lifetime, and diffusion length.[1]

A description of these imperfections, plus their detection and identification with particular application to germanium is given elsewhere[2]. General methods of preparing single crystals of salts and metals are discussed by Buckley and others.[3] The so-called Bridgman[4] technique of preparing single crystals in a mold by slowly lowering the crucible through a thermal gradient is inappropriate for substances (such as Ge and Si) which expand on freezing, since the confining walls tend to strain the freezing solid, often causing it to twin and become polycrystalline. This difficulty can be avoided by three convenient means: (a) crystals can be grown from the vapor phase by thermal decomposition of a volatile compound (such as a halide or a carbonyl) and consequent deposition of the metal on a hot wire (Van Arkel method[5]); (b) crystals can be grown by passing a very shallow or open crucible containing the molten germanium horizontally through a thermal gradient (Kapitza method[6]); (c) crystals can be grown from the melt by touching a single crystal seed to the liquid surface and slowly withdrawing it (Czochralski method[7]). All of the above methods have been used for the preparation of germanium single crystals. The present bulletin discusses the last method, which is readily used to prepare large germanium single crystals of any desired purity, and free of the above-mentioned gross imperfections along their entire length. Silicon, because of its higher melting point, (1420°C vs 935°C for germanium) is much more difficult to handle, but the same apparatus has been successfully used. This bulletin, however, will emphasize the germanium application.

Procedure

One type of apparatus used to grow single crystals of germanium and of silicon is shown in Figs. 1 and 2. It consists of a fused quartz* tube, 18 inches by 1½ inches, with a viewing side arm, held in Wilcox and Babcock No. 30

*If the furnace is to be used only for germanium, Vycor may be substituted for fused quartz in the apparatus.

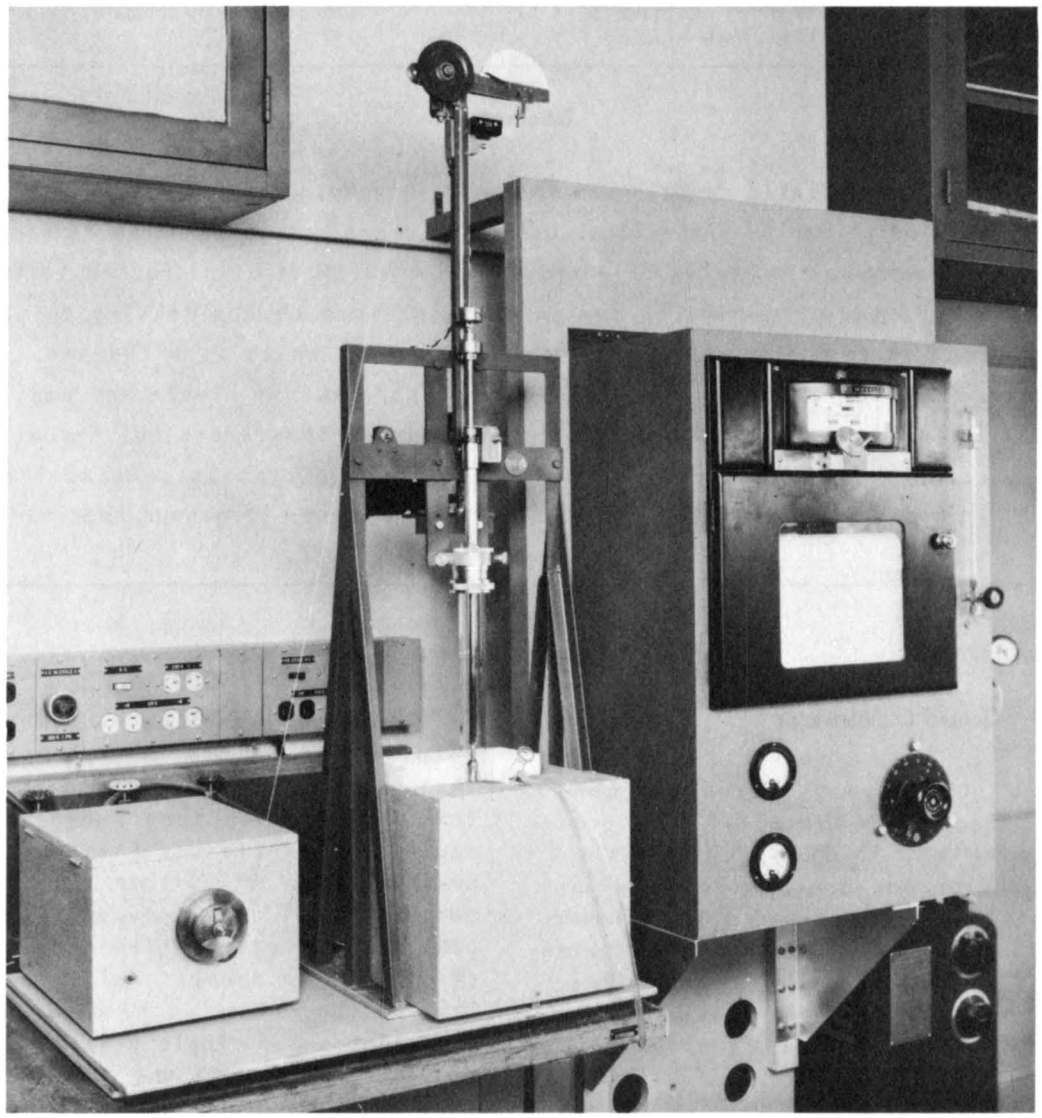

Fig. 1 – Photograph of crystal growing furnace equipped with viewing tube.

firebrick and heated by Globar (SiC) resistance heaters. The temperature, as noted by a thermocouple placed against the fused quartz tube, is regulated by a Wheelco controller type No. 7002-5 and kept to a small range, preferably under 1 degree C, by high-low rather than on-off regulation. The regulator is seen at the right of the furnace in Fig. 1. A germanium charge of from 30 to 330 grams contained in graphite crucibles varying in depth from 1 inch to 4 inches is placed in the bottom of the tube. Silica crucibles or liners are used for silicon work. A properly oriented single-crystal seed is clamped to a stainless steel holder which extends through the tube cap. An inert gas such as argon or helium is passed through the system at a sufficiently rapid rate to prevent smoking or oxidation. The germanium is melted and then slowly cooled until freezing just begins, after which the heat is again quickly applied to avoid cracking the crucible. Care is taken to note the temperature at which freezing begins. After the germanium has been remelted (at about 100 degrees over the above-noted freezing point) the temperature is reduced close to, but above, the freezing point. The seed, which is first preheated by holding it approximately 1/8 inch above the melt, is brought into contact with the liquid. Under proper conditions, as described above, the melt starts to solidify onto the seed thereby extending the crystal lattice of the seed downward. The seed is then

continuously raised until the liquid is converted into a single crystal rod.

The crystal grows because of a thermal gradient. If there is sufficiently uniform heating, the crystal growth is straight, but a relatively cold spot in the furnace causes the crystal to grow more rapidly in that direction. Rotation of the crystal will overcome any nonuniform heating and permit the crystal to grow uniformly. For this reason, rotation is provided for but, of course, can be turned off at will. Ordinarily, the growing crystal is raised slowly at approximately 1 mm/minute and turned at approximately 15 rpm, but each rate is variable and independent of the other. To indicate the possible range, a particular single crystal of germanium has been grown in which the pulling speed was varied from 0.25 to nearly 10 mm/minute and the turning speed was varied from zero to nearly 1000 rpm.

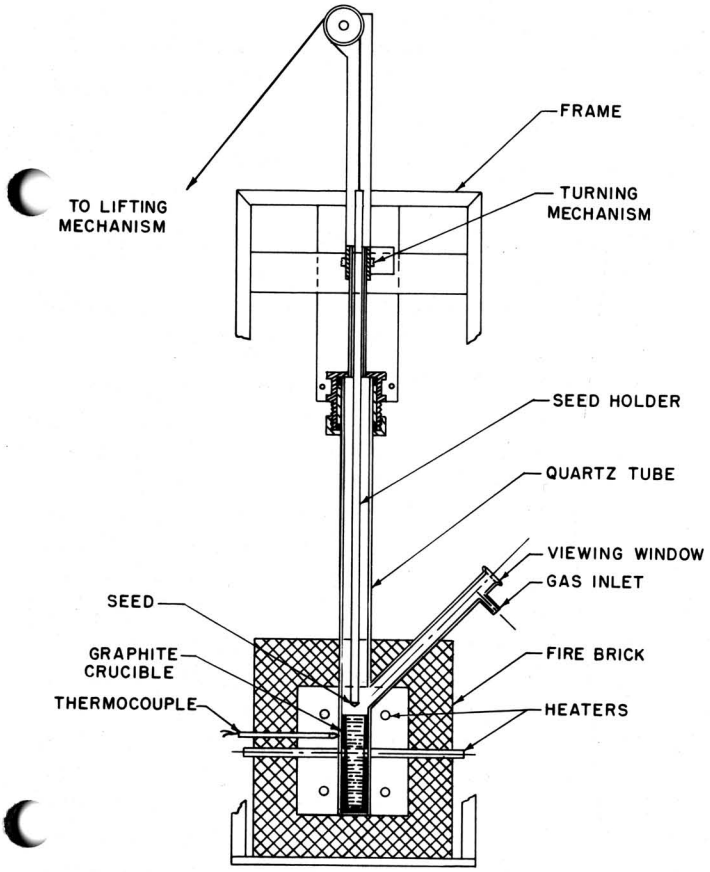

Fig. 2 - Cross-section drawing of furnace shown in Fig. 1.

A second crystal-growing apparatus is shown in Figs. 3 and 4. In this case, the viewing arm is eliminated to aid in obtaining a uniform heat gradient about the growing crystal axis, thus producing more uniform crystals and thereby facilitating automatic control. The wider tube ($2\frac{1}{2}$ inches OD) permits a better view of the liquid-solid interface throughout the process and permits the production of larger crystals. The simple open-end cylinder of fused quartz requires very little fabrication compared with that of Figs. 1 and 2. However, the furnace of Figs. 1 and 2 is more

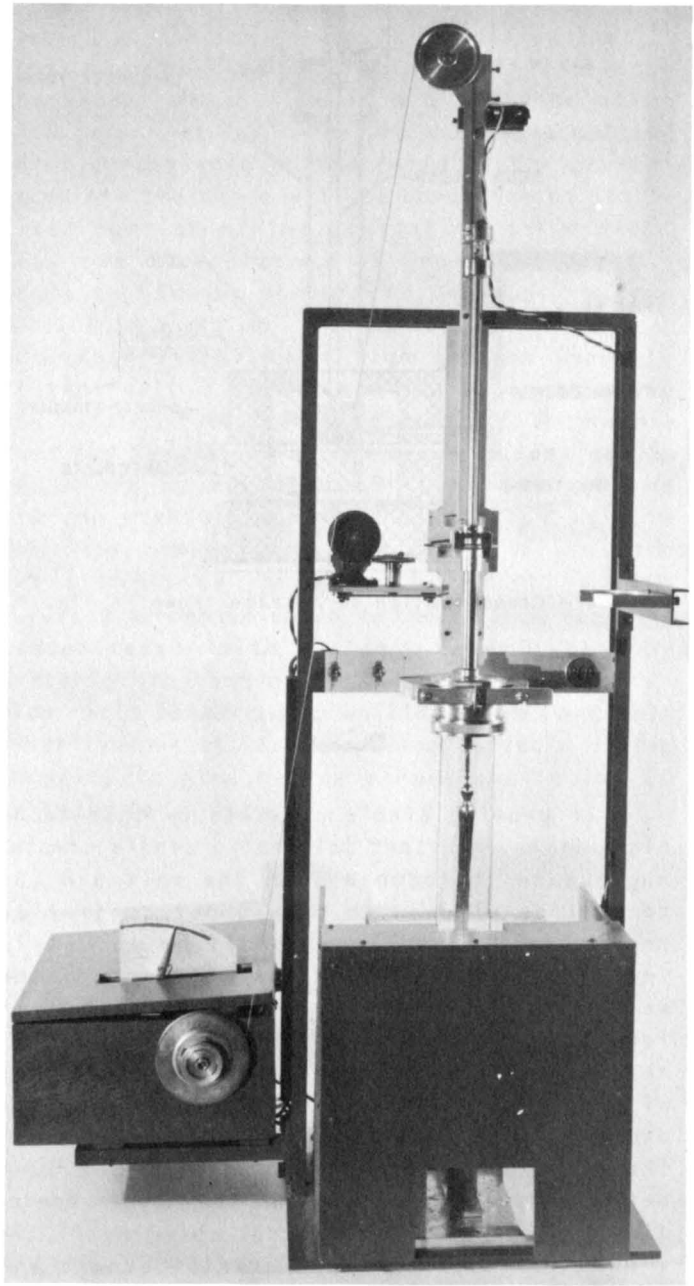

Fig. 3 - Photograph of symmetrical crystal growing furnace.

convenient for viewing the liquid surface and provides a gas-tight seal at the bottom.

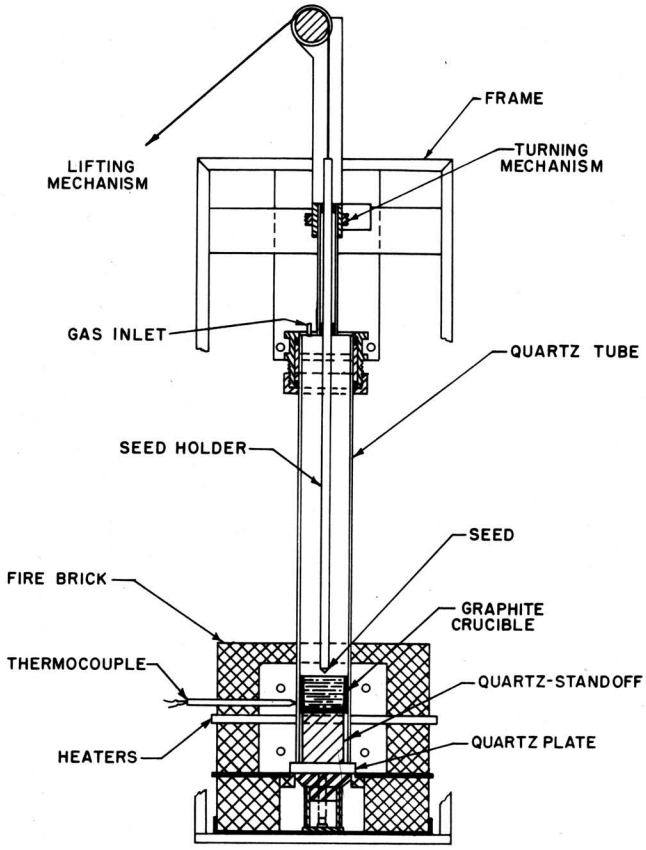

Fig. 4 - Cross-section of furnace shown in Fig. 3.

Discussion

In growing single crystals by this technique it is important (a) that a *single* crystal nucleus be introduced into the melt and (b) that it be allowed to grow under controlled conditions. To satisfy condition (a) it is important that, prior to the contact of the seed with the melt, the melt be heated at least 100 degrees above the melting point to reduce the size of the clusters or aggregates of atoms in the liquid and thereby minimize the probability of self-nucleation. Also, preheating the seed and dipping it into the melt just before the melt has cooled to the proper operating temperature will prevent chilling of the liquid followed by rapid crystal growth and will also effect a continuous joint between the seed and the new crystal. To satisfy the condition (b), it is essential that a close balance be maintained between the heat losse and the heat input in the neighborhood of the liquid-solid interface. If these are balanced, the crystal will grow with uniform cross section; if the heat input is excessive the cross section will decrease; and if the heat loss is excessive the cross section will increase.

Factors which affect the heat balance and thereby the diameter of the growing crystal are:

1. Furnace design (extent of insulation, radiation shielding, etc.)
2. Temperature of the melt.
3. Amount of melt (i.e., heat capacity).
4. Diameter of the seed.
5. Temperature of the seed (depends on diameter, length within the crucible, within the firebrick and above the firebrick).
6. Position and area of liquid surface (relative to the Globars and the firebrick).
7. Position and area of liquid-solid interface.
8. Rate of crystal withdrawal.
9. Rate of gas flow.
10. Physical properties of the material:
    a. Latent heat of fusion
    b. Thermal conductivity of the solid
    c. Thermal conductivity of the liquid

All of the factors listed above contribute to the thermal gradient across the liquid-solid interface. When the crystal is growing normally, that is, when steady-state conditions exist at the liquid-solid interface, the crystal obviously will grow thinner as the pulling rate is increased and will grow thicker when the rate is decreased. The crystal will also grow thinner and rounder as the melt temperature is raised; conversely as the melt temperature is lowered the crystal will grow thicker and develop the cross section and number of flats which are characteristic of a single crystal grown in a particular crystallographic direction. Thus, crystals grown in the 111 direction will have triangular cross section and show three flats at 120 degrees (except when thickening rapidly, when the cross section becomes hexagonal with six flats showing at 60 degrees); crystals grown in the 100 direction will have square cross section and show four flats a

90 degrees, etc. In growing single crystals of germanium and silicon by this technique, the singleness and crystallographic direction of the growing crystal is at once ascertained by the number and symmetry of the flats.

It has been shown[8] that grown crystals of certain metals will be single if the ratio of the thermal gradient to the growth rate is relatively high, and also if the thermal gradient is low. The optimum growth rate will depend on crystallographic direction, generally increasing as the growth direction changes from the 111 to the 110 to the 100 direction. Often when the growth conditions are not correct, sufficient stress is introduced into the system to cause the crystal to twin. Thereafter the crystal may continue to grow but with a different orientation. This is evidenced by a twin line which runs diagonally across the crystal, with a single crystal portion above and below the twin plane, each portion showing the characteristic number and symmetry of flats. The identification of the twin boundary is aided by the fact that diamond-type-lattice crystals almost invariably twin on the 111 plane.[9] The 111 plane in germanium and silicon is the plane of greatest separation, the most densely packed plane, the weakest plane, and the plane of easiest fracture or shear.[10]

With certain conditions of crystal growth, the crystal may develop dendritic or lineage patterns. If the melt temperature is too low, rapid dendritic growth occurs giving rise to dendritic patterns which are characterized by a regular herringbone pattern on the surface of the single crystal. If the crystal is drawn rapidly from a cool melt, lineage growth occurs which is characterized by long grains running the length of the crystal; the grains are all pointed in the same crystallographic direction down the crystal but are slightly misoriented with respect to each other.

When a crystal is melted and recrystallized, fractionation of impurities occurs[10,11]. Those impurities which form a eutectic type system and therefore lower the melting point of germanium concentrate in the melt as the crystal grows and therefore will be concentrated in the portion of the crystal which solidifies last[12]; those high melting impurities, namely silicon and boron, which also form a solid solution with germanium and therefore raise its melting point concentrate in the solid as the crystal grows and therefore will be concentrated in the first portion of the crystal to solidify.[13] Thus the very process of growing a crystal tends to make it nonuniform in impurity content.[14] In addition, it has been observed that alternating regions of high and low impurity content called striations may be found along the length of the single crystal.[15] The magnitude and separation of these striations can be minimized by agitation of the melt and the growing crystal. A single crystal of uniform impurity content and, therefore, of uniform resistivity can be grown by starting with purified germanium doped to the desired impurity concentration with a single impurity and by suitable programming of the following: agitation, melt temperature, pulling speed, and melt impurity content. Antimony is a suitable doping impurity to give n-type germanium; indium is suitable for p-type.

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