Single Crystals of Exceptional Perfection and Uniformity by Zone Leveling

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The zone-leveling process has been developed into a simple and effective tool, capable of growing large single crystals having high lattice perfection and containing an essentially uniform distribution of one or more desired impurities. Experimental work with germanium is discussed, and the possibility of broad application of the principles involved is indicated.

INTRODUCTION

The first publication describing the concept of zone melting appeared about four years ago.[1] As there defined, the term zone melting designates a class of solidification techniques, all of which involve the movement of one or more liquid zones through an elongated charge of meltable material. This simple concept has opened a whole new field of possibilities for utilizing the principles of melting and solidification.

The first zone melting technique to gain widespread usage was one for zone refining germanium by the passage of a number of liquid zones in succession through a germanium charge. This process may be quite properly compared to distillation, the essential difference being that the change in phase is from solid to liquid and back, instead of from liquid to vapor and back. The zone refining technique has been eminently successful in the purification of germanium. Harmful impurity concentrations are of the order of one part in 10^{10}. This is mainly because all the impurities whose segregation behavior in freezing germanium has been measured have segregation coefficients (see equation 1) differing from 1 by an order of magnitude or more.[2] During the zone refining operation, these impurities collect in the liquid zones and are swept with them to the ends of the charge, which may be later removed.

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[1] Pfann, W. G., Trans. A.I.M.E., **194**, p. 747, 1952.
[2] Burton, J. A., Impurity centers in Germanium and Silicon, Physica, **20**, p. 845, 1954.

This paper deals with a second zone melting process, zone leveling,[1, 3] which has gained usage somewhat more slowly than zone refining, but which has proved to be a highly effective tool for distributing desired impurities uniformly throughout a charge. For this process, only one liquid zone is used and its composition is adjusted to produce the desired impurity concentration in the material which is solidified from the liquid zone. Appropriate precautions are taken to insure the production of single crystals, if the material is desired in this form.

Since the invention of zone leveling, the process has been developed into a precision tool and as such it has become a preferred practical method for growing germanium single crystals of uniform donor or acceptor content. It is the purpose of this paper to discuss the technical development of this process, which has had two chief objectives: (1) the attainment of the greatest possible uniformity of donor and/or acceptor impurity distribution in the crystal; and (2) the attainment of a germanium crystal lattice with a minimum of imperfections of all kinds. The presentation will cover the principles involved, the means developed and results achieved toward these objectives in that order.

The first applications of the principles of zone melting have been in the field of semiconductor materials processing, chiefly because there are no other known refining techniques capable of meeting the extremely stringent purity requirements necessary for material to be used in semiconductor devices. Nevertheless, it is clear that these relatively simple and very effective zone melting techniques are beginning to find a wide variety of useful applications throughout the general fields of metallurgy and chemical engineering.

BASIC PRINCIPLES

The basic concept, theory and experimental confirmation of zone leveling have been well covered in previous publications.[1, 3] Accordingly, the intention here is only to repeat the salient points of the theory with a special emphasis on the assumptions involved since it will be necessary to refer to them.

Fig. 1 is a schematic drawing of a zone leveling operation showing a liquid zone of constant volume containing a solute whose concentration is C_L. As the zone moves a distance Δx an increment of germanium is melted at the right end, and another is frozen at the left end. The concentration of solute in the newly frozen Δx of solid solution is C_s. The distribution coefficient k is now conveniently defined as the ratio

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[3] Pfann, W. G., and Olsen, K. M., Physical Review, **89**, p. 322, 1953.

of these solute concentrations:

$$k = \frac{C_s}{C_L} \tag{1}$$

When $k < 1$, the freezing interface may be regarded as a filter permitting only a fraction k of the solute concentration in the liquid to pass into the growing solid and rejecting the rest to remain in the liquid. If the unmelted charge of solvent is pure — that is, if no solute passes into the zone at the melting interface it is readily seen that the liquid zone will be gradually depleted of its solute impurity content during passage through the charge.

An expression for the solute concentration in the solid, C_s, deposited there by the passage of one zone, for the case of "starting charge into pure solvent" has been derived[1] based on the following assumptions:

(1) The liquid volume is constant (both cross section of charge and zone length l are constant).

(2) k is constant.

(3) Mixing in the liquid is complete (i.e. concentration in the liquid is uniform).

(4) Diffusion in the solid is negligible.

The expression is

$$C_s = kC_{L_0} e^{-kx/l} \tag{2}$$

where C_{L_0} is the initial concentration of impurities in the liquid, l is the zone length, and x is the distance moved by the solidifying interface. A set of C_s versus x/l curves is shown in Fig. 2 for various k's. From this figure it is readily seen that when k is small the decay of C_s is slow (i.e., the depletion of C_L is slight).

Largely because of this consideration, most of the practical work reported in this paper has utilized solutes in germanium having low segre-
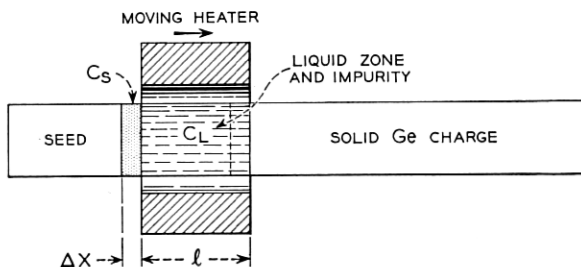

Fig. 1 — Schematic of zone leveling operation.

gation coefficients (usually antimony, whose $k = 0.003$ as donor, and indium whose $k = 0.001$ as acceptor). However, the principles of zone leveling are broad and capable of application to any solvent-solute system within the range of solubilities of its solid and liquid phases. The general method of attack[1] is first to find that composition of the liquid zone which will deposit the desired solid solution. Secondly, if one or more of the segregation coefficients involved is not small, the liquid zone must be maintained at its proper composition by admixing to the solid charge the same solutes that the zone will deposit in its product. Thus the solutes that are removed from the liquid zone at the freezing end will be replenished at the melting end.

The above mathematical treatment leads one to expect an essentially uniform solute distribution throughout a zone leveled crystal for the case under discussion in which k is small and the zone moves through a charge of pure solvent as indicated in Fig. 2. Irregular variations of C_S along the length or over the cross-section of the ingot are not predicted. The
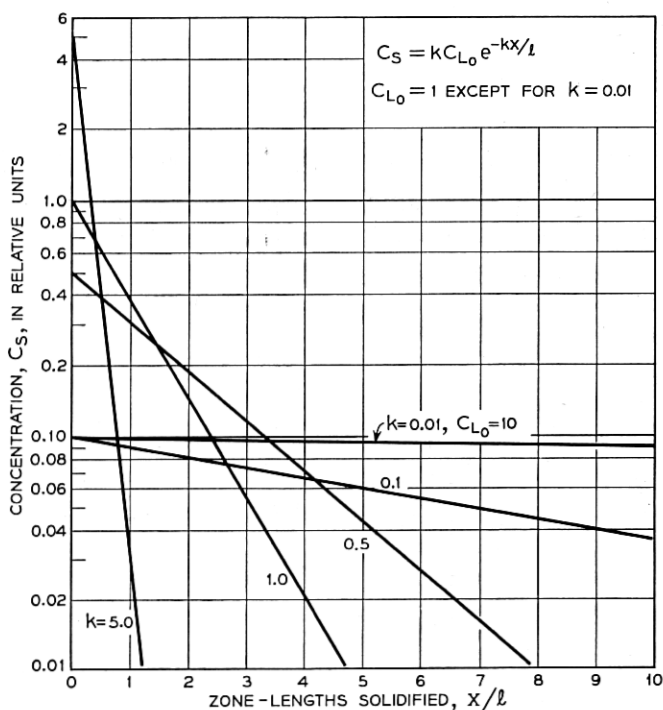

Fig. 2 — Solute concentration curves predicted for zone leveling with a starting charge of solute into pure solvent.

treatment is not concerned with lattice imperfections in the ingot such as dislocations, lineage, or grain boundaries. The predictions the theory does make have been well verified by experiment insofar as it has been possible to meet the assumptions enumerated above. However, as with most assumptions, their validity is sensitive to the experimental conditions, particularly in the cases of the first three. Much of the development effort, especially that toward improving resistivity uniformity, has been directed toward controlling the process so that these assumptions will be as nearly valid as possible.

Early experiments in zone leveling yielded crystals good enough to meet device requirements of that time. However, as semiconductor devices were designed to meet tighter design requirements, the demands on the germanium material grew more critical. Under these circumstances, it became necessary to examine the requirements on the product of the process and what precautions would be necessary to insure that its operation was under sufficient control. Accordingly, we shall discuss first the requirements on semiconductor material and then those critical aspects of the leveling operation which must be controlled to insure quality of the final product.

REQUIREMENTS ON GERMANIUM FOR SEMICONDUCTOR USES

The basic electrical bulk property of a germanium crystal is its conductivity or the reciprocal of that quantity, its resistivity. For a great majority of semiconductor uses, an extrinsic conductivity[4] is required in addition to the $\frac{1}{50}$ ohm^{-1} cm^{-1} intrinsic conductivity that results at room temperature from thermal excitation of electron-hole pairs in pure germanium. An extrinsic conductivity may be either n-type or p-type. Both of these may be produced by trace impurities distributed throughout the crystal, the n-type by donor impurities and the p-type by acceptor impurities. At room temperature donors give rise to conduction electrons and the acceptors to conduction holes which are free to move within the germanium crystal. If both donors and acceptors are present in the same crystal, the resulting electrons and holes recombine, leaving essentially the extrinsic conductivity contributed by the excess of one over the other, that is by $| N_D - N_A |$.

The fundamental requirement is, then, to control the net donor and the acceptor balance, $| N_D - N_A |$, to a predetermined value throughout the crystal. For most applications, the conductivity is to be increased by one or two orders of magnitude above the 27°C intrinsic value. An idea of the donor or acceptor concentrations involved may be acquired

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[4] Shockley, W., Electrons and Holes in Semiconductors.

from noting that a conductivity of $\frac{1}{5}$ ohm^{-1} cm^{-1} (that is, a conductivity increased by one order of magnitude) corresponds to a $N_D - N_A$ concentration of 7 parts per billion.

The next most commonly measured bulk property of germanium is the lifetime of minority carriers,[5] i.e., the time constant for decay by recombination of a surplus population of minority carriers artificially introduced into the crystal. Minority carriers are holes in n-type germanium or electrons in p-type germanium. This time constant may be regarded reasonably as a figure of merit for the crystal, being an indication of its freedom both from certain chemical impurities and from crystal faults, since these act as catalysts to the electron-hole recombination reaction. Normally, the highest possible lifetime is desired. Thus it becomes important to take extreme precautions during handling and processing of the germanium to avoid contamination, particularly by such known recombination center elements as nickel and copper[6] and it is also important to avoid crystal lattice faults such as dislocations, lineage, and grain boundaries.

Another observable quantity has recently been gaining acceptance as a more definite indication of mechanical crystal perfection than the minority carrier lifetime measurement. This is the etch pit density count, ϵ, (see Fig. 3) which is observed microscopically on an oriented (111) surface of a Ge crystal that has been etched three minutes in an agitated CP-4 etch (20 parts by volume concentrated HNO$_3$, 12 parts concentrated HF, 12 parts concentrated acetic acid, and $\frac{1}{2}$ part Br$_2$). There is strong evidence[7] that the etch pits are formed at the intersections of dislocations with the surface of the crystal. While an etch pit count probably indicates only certain edge dislocations which intersect the surface of the crystal, it is at least a relative indication of the total dislocation density, and thus appears to be a highly useful index of crystal lattice perfection.

In the last year, evidence of a strong correlation has been observed[8] between certain electrical properties of alloy junctions, especially the breakdown voltage, and the etch pit density of the material on which the alloy junction is made. Accordingly, material to be used for alloy junction transistors is now selected on the basis of its maximum etch pit count and its freedom from lineage, twin, and grain boundaries.

The usual device test requirements on n- or p-type Ge material vary

[5] Valdes, L. B., Proc. I.R.E., **40**, p. 1420, 1952.
[6] Vogel, F. L., Read W. T., and Lovell, L. C., Phys. Rev., **94**, p. 1791, 1954.
[7] Vogel, F. L., Pfann, W. G., Corey, H. E., Thomas, E. E., Physical Review, **90**, p. 489, 1953.
[8] Zuk, P., and Westberg, R. W., private communication.

Fig. 3. — Microphotograph of Typical Etch Pits on (111) Plane.

from device to device, but may be summarized as follows:

(1) *Composition* — The donor-acceptor balance $N_D - N_A$ must be accurately controlled so that the resistivity, ρ, of the crystal is uniform and falls within acceptable tolerance limits.

(2) *Macro Perfection* — The crystal shall contain no grain boundaries, lineage, or twinning.

(3) *Micro Perfection* — The etch pit density, ϵ, must be lower than a certain empirically determined maximum.

(4) *Lifetime of Minority Carriers* — τ, must usually be above a certain minimum, although in many cases this minimum may be as low as a few microseconds.

Assuming macro perfection a consideration of these requirements leads directly to the two general objectives mentioned in the introduction of this paper: composition uniformity and control, and crystal lattice perfection. A third objective, high chemical purity, might also be inferred from the lifetime requirement, but the results obtained by zone refining raw material and by fairly standard laboratory techniques of cleaning and baking of furnace parts at high temperature have been satisfactory. Hence this objective has required little development effort. We proceed to a discussion of critical aspects of zone leveling in the light of the two major development objectives.

COMPOSITION UNIFORMITY AND CONTROL

The experimental development work described in this paper has been concerned with the distribution of two trace impurities, indium and anti-

mony, in a pure element, germanium. The traces are generally desired in concentrations varying from 1 to 100 parts per billion, ($\rho = 35$ to 0.35 ωcm). These amounts are too small to be detected by chemical or spectrographic means, but are readily detectable by electrical resistivity measurements. Although this application of zone leveling is very specific, it should be possible, as we have already suggested, to apply the experimental results to be described to more general systems. The subject of uniformity is conveniently discussed in two sections: (a) longitudinal resistivity uniformity, and (b) cross-sectional uniformity.

(a) *Longitudinal Composition Uniformity*

It has already been shown, by (2), that if the k is small, the variation in C_S over four or five zone lengths should be slight. This should be true either if a charge of pure germanium is used, or if a charge containing the same impurity present in the liquid zone is used, provided that the charge concentration of this impurity is of the same order of magnitude as that sought in the product. Where the solute has a small k, the leveling action of the zone is strong and the large C_L that is required is relatively unaffected by variations of the order of C_S.

The primary cause of observed variations in the *longitudinal* resistivity is fluctuation of the volume of the liquid zone. If this volume increases for any reason, the solute dissolved in it will be diluted. On the other hand, if the volume decreases, which can occur only when some of the liquid freezes and if k is small, most of the zone's solute will be concentrated in the smaller volume. Thus for small k's the concentration of solute in the liquid zone, C_L, varies inversely with the zone's volume. If C_L is to be constant, the volume must be constant, i.e. assumption (1) must be valid.

Unfortunately, the zone volume is directly affected by many variables, namely temperature fluctuation and drift, fluctuation in growth rate, variation in the cross-section of the unmelted charge, variation in the inert gas flow, and even cracks in the unmelted charge. For optimum control of longitudinal resistivity uniformity, it is, therefore, necessary to control all of these variables. The remainder of this section will consider their control.

Toward minimizing the effect of temperature variation on the zone volume, it is important to consider both the means of overall temperature control and the design of the temperature field which melts the liquid zone. It is clear that variation of the temperature field as a whole will directly affect the length of the liquid zone. Accordingly, it will be important to use a precision temperature controller in order to maintain a

constant zone length. The controller used here is a servo system that cycles the power on and off about ten times a second, adjusting the on fraction of the cycle according to the demands of a control thermocouple. The sensitivity of the controller is ±0.2°C at 940°C. With a liquid zone about 4 centimeters long and a temperature gradient of about 10°C per centimeter at the solidification interface, this degree of control should introduce longitudinal resistivity variations no greater than ±0.3 per cent.

When other requirements permit, it is possible to design a temperature contour to minimize the effects of control fluctuations. When the temperature gradients at the ends of the liquid zone are small, a slight change in the general temperature of the system will cause a relatively large change in the position of the solid-liquid interface. On the other hand, when the gradient is steep, the shift in position of the interface will be small. It is with this consideration in mind that a temperature gradient of about 130°C/cm is provided at the melting end of the liquid zone (Fig. 4). A steep gradient has the added advantage that it provides a large heat flux which is capable of supplying or removing the heat of solidification even at relatively fast leveling rates. Thus, a steep temperature gradient serves effectively to localize a solid-liquid interface. Other considerations, soon to be discussed, dictate that a small temperature gradient (about 10°C/cm) must be used at the freezing end of the zone. Accordingly, high precision of temperature control is required to properly stabilize the position of this solid-liquid interface.

Variation in the cross-section of the liquid zone may be controlled by using a boat with uniform cross-section, and by using as charge material which has been cast into a mold of controlled cross-section. Less precise control is obtained by using ingots from the zone refining process which were produced in a boat matched to the zone leveler boat. Even when care is used to maintain a uniform height of the zone refined ingot,[9] the control is less precise than in a casting.

A constant and uniform growth rate is important toward obtaining uniform longitudinal resistivity because segregation coefficients vary with growth rate.[10] This is especially true in the case of the k for antimony. Under steady state conditions, the growth rate is the rate at which the boat is pulled through the heater. A stiff pulling mechanism is required in order that the slow motion be steady. In the apparatus described here, a syncronous motor, operating through a gear reduction to drive a lead screw, has served to pull the boat smoothly over polished quartz rods.

[9] Pfann, W. G., J. Metals, **5**, p. 1441, 1953.
[10] Burton, J. A., Kolb, E. D., Slichter, W. P., Struthers, J. D., J. Chem. Phys., **21**, p. 1991, Nov., 1953.
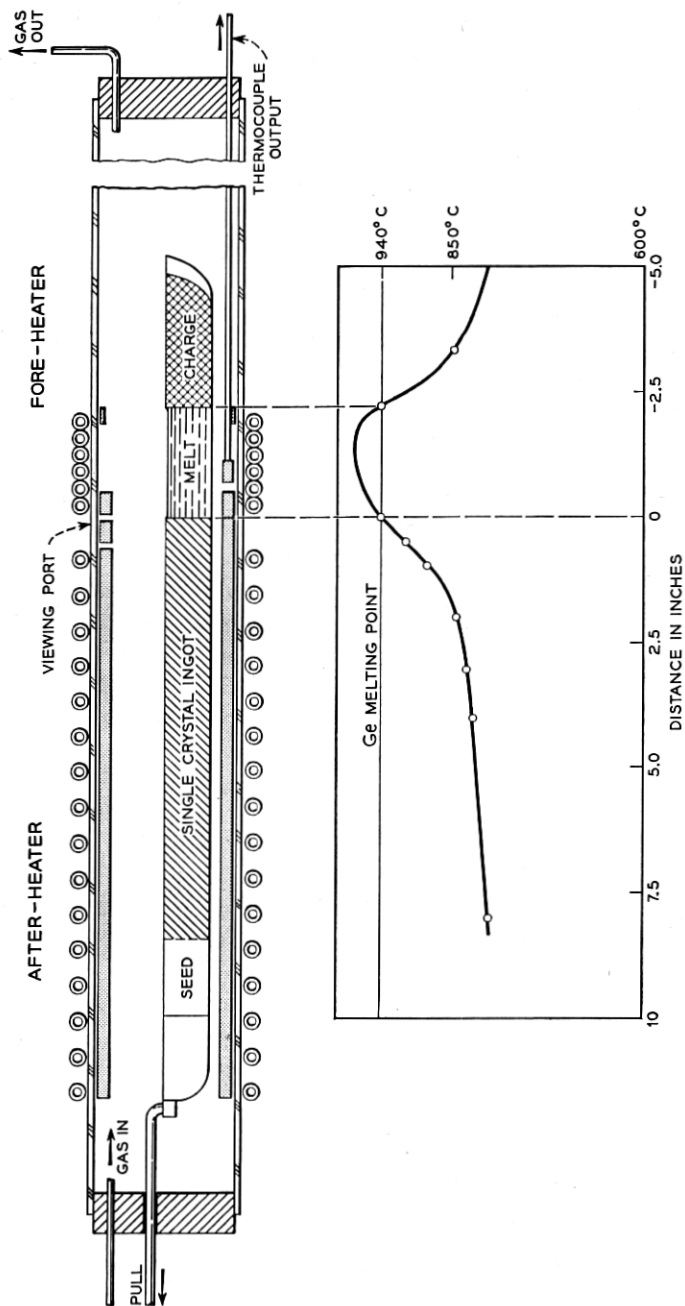
Fig. 4 — Axial temperature curve for the germanium zone leveler with after heater.

The true growth rate may be affected by factors that cause variations from steady state growth such as temperature and gas flow fluctuations. The need to control these variables has already been mentioned because of their effect on zone volume; their effect on growth rate is thus a second reason for their control.

Cracks or similar discontinuities in the unmelted charge act as barriers to heat flow. Thus they cause a local rise in temperature and lengthening of the liquid zone as the crack approaches the zone, until it is closed by melting. The resulting transient increase in liquid volume (and in ρ of the product) may be of the order of 10 per cent.

(b) *Cross-Sectional Composition Uniformity*

Difficulty may be expected in controlling the cross-sectional uniformity of the zone leveled ingot chiefly when the third assumption is invalid, i.e., when C_L throughout the liquid is non-uniform. As shown in the next paragraph, the true C_L must always rise locally near the solidifying interface due to the solute diffusion which is necessary when $k < 1$. However, it is possible to improve the validity of assumption 3 both by slowing the growth rate and by stirring the liquid zone.

One can form an estimate of a theoretically reasonable growth rate in terms of the rate of diffusion of impurities in liquid germanium. It should be noted that movement of a liquid zone containing a solute whose segregation coefficient is small implies a general movement by diffusion of essentially all the solute atoms away from the solidifying interface at a speed equal to the rate of motion of the zone. Even slow zone motion corresponds to a high diffusion flux of the solute through the liquid. As a consequence, the solute concentration must rise in front of the advancing solidification interface to a concentration $C_{L'}$ (see Fig. 5) until a concentration gradient is reached sufficient to provide a diffusion flux equal to the growth rate. Fick's Law of diffusion is useful here to calculate the extent of the rise in $C_{L'}$ at the growth interface, assuming the liquid to be at rest. The ratio of the maximum concentration to the bulk concentration may be taken from Fig. 5. If the maximum is to be no greater than 10 per cent above the mean, a maximum growth rate of 2×10^{-7} mils per second or 7×10^{-7} inches/hour would be required. Clearly, this rate is far too slow to provide an economical means of growing single crystals. For a practical process, it will be necessary to use non-equilibrium conditions at growth rates that must result in appreciable concentration differences within the liquid zone. Of course, the slower the growth rate the smaller will be the diffusion gradient and the higher will be the expected cross-sectional uniformity.
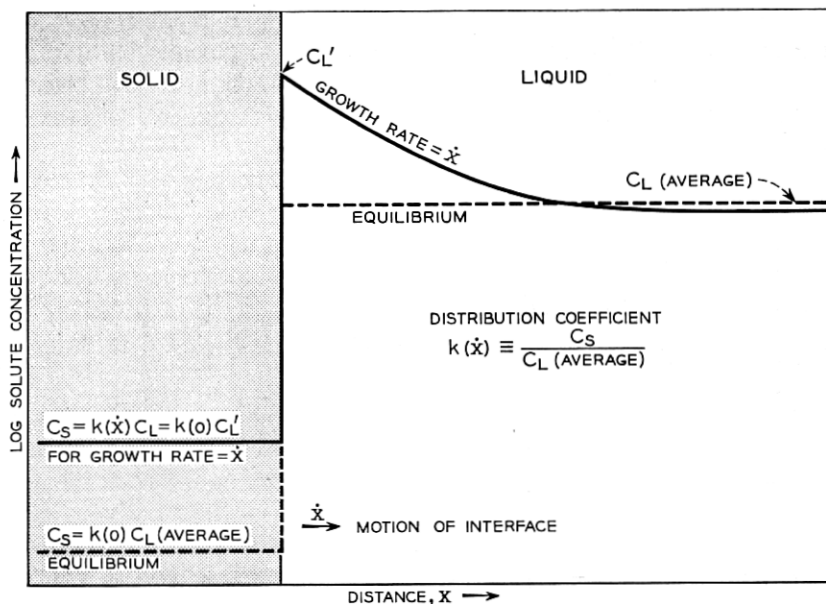
Fig. 5 — Solute concentration in solid and liquid at equilibrium and at finite growth rates.

If the liquid were static, that is, without any currents, it should be possible to obtain a uniform, controlled solute concentration in the solid even at appreciable growth rates, merely by adjusting the average concentration in the liquid to arrange that the C_L obtained at the growing interface will be the desired one. Instead of working with the equilibrium distribution coefficient k_0, one works with an effective distribution coefficient $k(\dot{x})$ for the given growth rate, $\dot{x}$:

$$k(\dot{x}) = \frac{C_s}{C_L(\text{ave})} \qquad (3)$$

In practice, however, the situation is complicated by the existence of convection currents in the liquid zone. It is true that these currents tend to stir the liquid zone and thereby to minimize the concentration gradient within it. However, the currents are not uniform over the growing interface and they carry liquid of varying concentrations past the interface, causing fluctuations in C_s. Since these convection currents cannot be eliminated, one turns to the alternative of using forced stirring of the liquid zone. Such a forced stirring is readily available when RF induction heating is used by allowing the RF field to couple directly with the

liquid zone.[11] The resulting stirring currents are shown schematically in Fig. 6. It is seen that the liquid is moved from the center of the zone along its axis toward both ends. There it passes radially outward across the interface and returns along the outside of the zone to its center. These stirring currents are faster than convection currents and tend to minimize the rise of C_L at the solidification interface and to improve the uniformity of C_L and of crystal growth conditions in general over the freezing interface.

CRYSTAL LATTICE PERFECTION

A single edge dislocation in germanium may be regarded as a line of free valence bonds. The dislocation line is believed to have about 4×10^6 potential acceptor centers per centimeter, producing a space charge in the neighboring germanium and strongly modifying its semiconductor properties.[12] A lineage boundary (a term found useful to designate a low angle grain boundary) is a set of regularly spaced dislocations, and may be regarded as a surface of p-type material. Since the basic electrical properties of a semiconductor, resistivity (and also minority carrier lifetime) are drastically out of control at dislocations and arrays of dislocations, it is easy to understand why these lattice imperfections are undesirable in crystals to be used for most semiconductor purposes.

The attainment of high perfection in germanium lattices may conveniently be discussed in two parts: first, the growth of a single crystal of high perfection and, second, the preservation of the crystal's perfection during its cooling to room temperature.

The problem of growing a single crystal in the zone leveler is basically one of arranging conditions so that the liquid germanium solidifies only
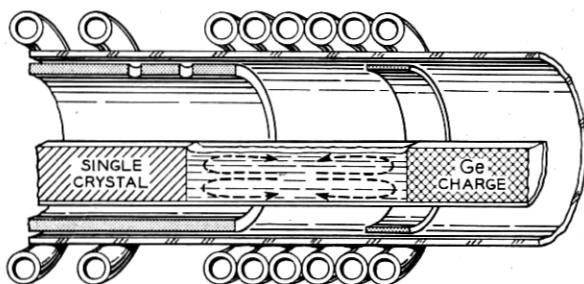

Fig. 6 — Stirring currents in liquid induced by RF induction heater.

[11] Brockmeir, K., Aluminium, **28**, p. 391, 1952.
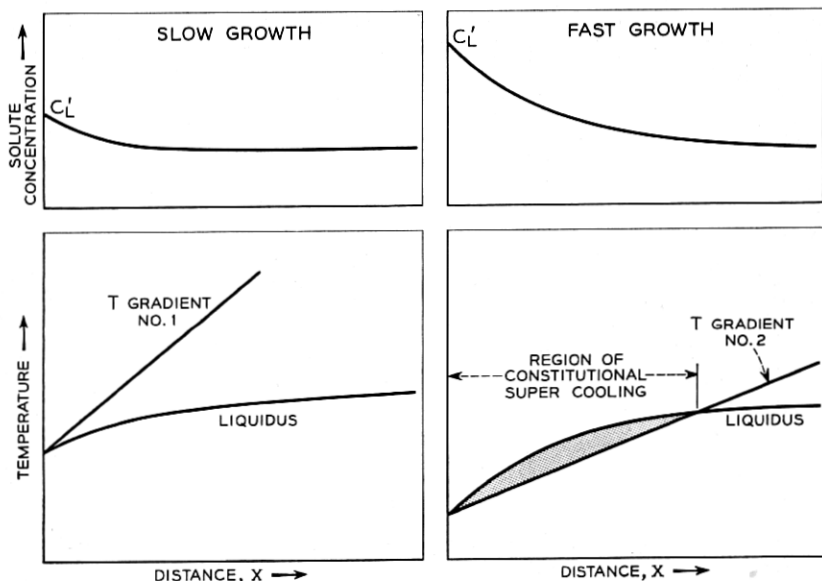[12] Read, W. T., Phil. Mag. **45**, p. 775, 1954.

Fig. 7 — Schematic solute concentration and temperature curves in liquid, near freezing interface, illustrating constitutional supercooling. The left edge of each diagram represents the solid-liquid interface.

on the single crystal germanium seed. In order to achieve this situation, it is essential that no stable nuclei form. Thus, not only must the temperature of the liquid zone be above its freezing point everywhere except at the interface, but the liquid must also be free of foreign bodies that can ct as nuclei. Furthermore, temperature fluctuations are to be avoided.

The requirement that the liquid temperature be above its freezing point necessitates a slow growth rate because of what has been termed "constitutional supercooling."[13] This phenomenon can best be described with the aid of Fig. 7. The freezing point of a liquid is depressed by increasing concentration of solutes having k's less than unity. Because of the rise in C_L near the solidifying interface, the freezing point is more depressed in this region than that in the bulk of the liquid zone as shown in Fig. 7.

It has also been shown[14] for crystals growing in one dimension that the temperature gradient in the liquid decreases for increasing growth rates. The temperature gradients for two growth rates are plotted on Fig. 7. It can be seen that where the growth rate is slow and the temperature

[13] Chalmers, B., J. Metals, 6, No. 5, Section 1, May, 1954.
[14] Burton, J. A., and Slichter, W. P., private communication.

gradient is steep, the temperature of the liquid is above its liquidus (freezing point curve) throughout the liquid, and no stable nuclei can form. However, increasing the growth rate decreases the temperature gradient, while it depresses the liquidus. If the temperature gradient is reduced to that indicated for fast growth, a region of constitutional supercooling will exist in front of the solidifying interface where nuclei can form and grow. The freezing of such a crystallite onto the growing crystal marks the end of single crystal growth.

A foreign body may also initiate polycrystalline growth. A natural site for nucleation by foreign bodies is the wall of the boat, close to the growth interface. Here the liquid germanium is in contact with foreign matter at temperatures approaching its freezing point. It was found by D. Dorsi that germanium single crystals could be grown satisfactorily in a smoked quartz boat, at growth rates up to 2 mils per second. However, uniformity considerations mentioned previously make it desirable to zone level at much slower rates.

It is believed that scattered dislocations may be produced in a single crystal germanium lattice by three chief mechanisms. They may be propagated from a seed into the new lattice as it grows; they may result from various possible growth faults; but probably the most important mechanism in this work is plastic deformation of the solid crystal. The first cause may be minimized by selecting the most nearly perfect seeds available, the second by using slow growth rates, and the third by minimizing stresses in the crystal.

The first hint that plastic deformation in the crystal might be an important source of dislocations came from the study of crystals pulled from the melt by the Teal-Little technique. Frequently when sections of crystals grown in the [111] direction were etched in CP_4 the pits were arrayed in a star pattern, Fig. 8(a), in which the pits appeared on lines — not randomly distributed. This coherent pattern suggested strongly that the lines were caused by dislocations in slip planes which had been active in plastic deformation of the crystal. The slip system of germanium has been determined to be the $<110>$ directions on $\{111\}$ planes.[15] If the periphery of the crystal is assumed to be in tension, it is possible to calculate the relative shear stress pattern in each slip system of the 3 $\{111\}$ planes which intersect the (111) section plane. The results of these calculations are summarized in Fig. 8(b) which shows a polar plot of the largest resolved shear stresses for these planes and also their traces in the section plane. The agreement with the observed star pattern is striking.

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[15] Treuting, R. G. Journal of Metals, 7, p. 1027, Sept., 1955.
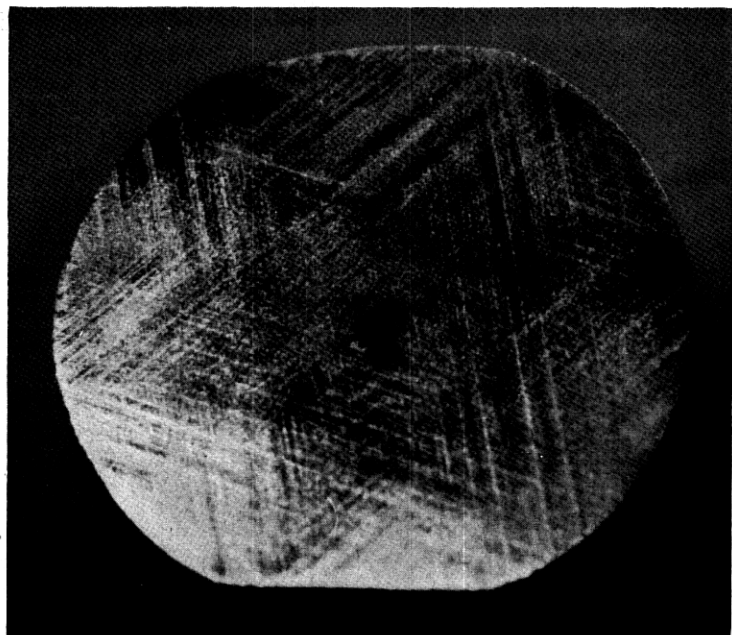
Fig. 8(a) — Star Pattern on (111) plane (etched cross-section of crystal pulled from melt).

The peripheral tension assumed in the above paragraph may be seen to be qualitatively reasonable upon consideration of the heat flow pattern of the crystal during growth. Heat must enter the crystal by conduction through its hottest surface, the growing interface, which is a 940°C isotherm. It must leave through all the other surfaces by radiation and conduction. Therefore, these surfaces must be cooler than their adjacent interiors, and cross-sections of the crystal must have cooler peripheries than cores because of the heat escaping from the peripheral surfaces. Due to thermal contraction the cooler periphery must be in tension and the core in compression.

In zone leveled crystals the distribution of etch pits on a (111) section was not dense or symmetric enough to display a star pattern. However, it was reasoned that since thermal contraction stresses appeared to play a major role in the production of dislocations in pulled crystals through plastic deformation in the available slip systems, the same mechanism might be playing a significant role in zone leveled crystals.

The only stresses in a zone leveled ingot other than those due to the weight of the crystal itself must be those due to non-uniformities in

thermal contraction. Consider a small increment of the length of a newly formed zone leveled crystal as heat flows through it from its hotter to its colder ends while the crystal moves slowly through the apparatus. Heat flows in by conduction from the higher temperature germanium adjacent to it. Heat leaves not only by conduction out the other end, but also by conduction and radiation from the ingot surface. Because of this latter heat loss, there is a radial component as well as a longitudinal component to the temperature gradient. The cooler surface contracts resulting, as above, in peripheral tension and internal compression. Clearly if the radial component of heat flow could be eliminated, there would be no peripheral contraction. Accordingly, the most desirable temperature distribution is one whose radial heat flow is zero, i.e., a case of purely axial or one dimensional heat flow, which implies a uniform temperature gradient along the axis of the ingot. In practice, it is difficult to obtain a uniform axial temperature gradient except for the special case of a very small one. This may be obtained fairly easily by the use of an ap-
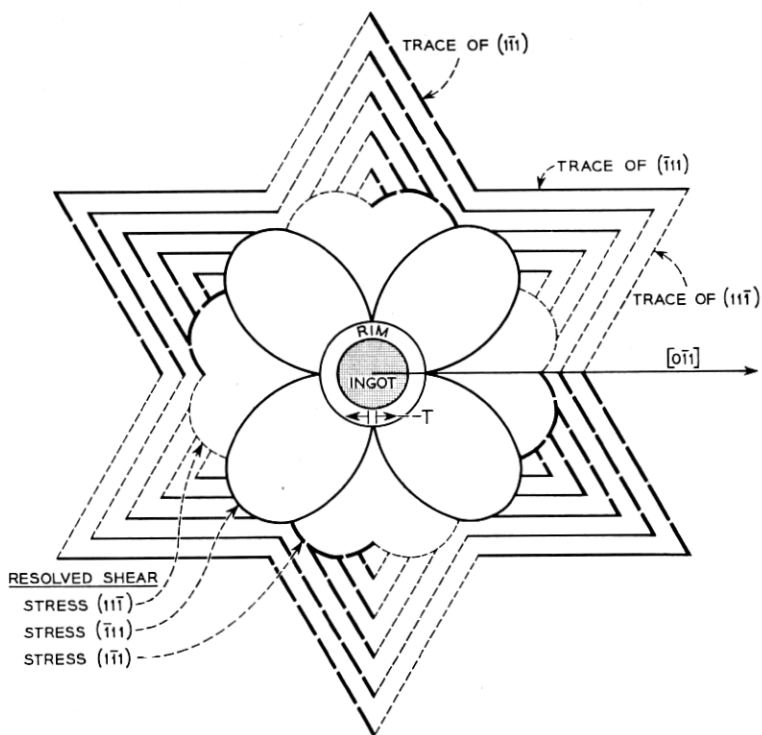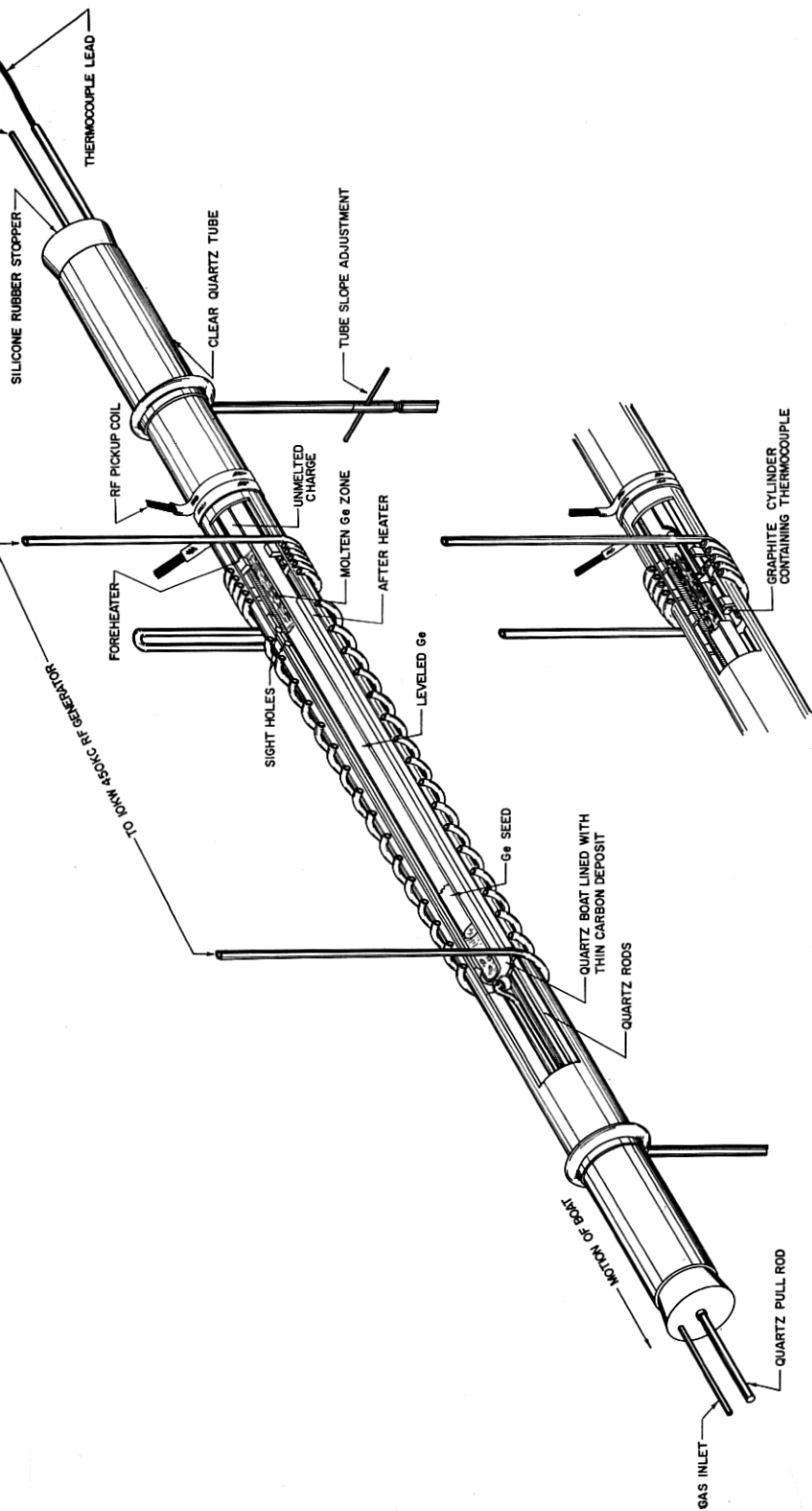

Fig. 8(b) — Resolved shear stress and slip-plane traces on (111) Plane.

THERMOCOUPLE LEAD

SILICONE RUBBER STOPPER

CLEAR QUARTZ TUBE

TUBE SLOPE ADJUSTMENT

RF PICKUP COIL

UNMELTED CHARGE

MOLTEN Ge ZONE

AFTER HEATER

FOREHEATER

SIGHT HOLES

LEVELED Ge

TO 10KW 450KC RF GENERATOR

Ge SEED

QUARTZ BOAT LINED WITH THIN CARBON DEPOSIT

QUARTZ RODS

MOTION OF BOAT

QUARTZ PULL ROD

GAS INLET

GRAPHITE CYLINDER CONTAINING THERMOCOUPLE

A—WITH AFTER HEATER

B—WITHOUT AFTER HEATER

Fig. 9 — Two views of a zone leveler. (a) With after-heater. (b) Without after-heater.

propriate heater. The heater designed for this purpose is called an after-heater and is shown in Figs. 4 and 9.

The after-heater reduces the heat loss by radiation and radial conduction from the crystal maintaining the entire crystal at a temperature only slightly below its melting point throughout its growth. After zone leveling has been completed, the entire ingot is cooled slowly and uniformly. Of course, a finite temperature gradient must exist at the liquid-solid interface. The gradient at the interface of the leveler shown in Figs. 4 and 9 is about 10°C per centimeter and the maximum gradient, about $\frac{1}{4}$ inch into the solid, is 30°C per centimeter. The gradient decreases slowly to nearly zero within the after-heater, as can be seen in the measured temperature curve of Fig. 4.

A ZONE LEVELING APPARATUS AND TECHNIQUE FOR GERMANUIM

The apparatus required for zone leveling is basically simple. A single crystal seed, the desired impurities, and a germanium charge, are held in a suitable container in an inert atmosphere. Provision is supplied for either moving a heater along the charge or the charge container through a heater. The heater may be either an electric resistance type or a radio frequency induction type. The resistance heater offers the advantage of economy while the induction heating offers the advantage of direct inductive stirring of the melted zone by the RF field, which, as mentioned previously, is helpful in attaining uniformity of impurity distribution, and is therefore to be preferred for critical work.

Schematic drawings of an RF powered zone leveler following in general the original design by K. M. Olsen are shown in Fig. 9 in two useful configurations. The outer clear quartz tube serves to support the inner members of the apparatus and also to contain the inert atmosphere for which nitrogen, hydrogen, helium, or argon, can serve. For this apparatus, a quartz boat is used to contain the germanium, since it permits inductive stirring of the liquid germanium by the RF field. The auxiliary fore and after heaters, which are made of graphite, have special purposes discussed in the two preceding sections. A typical boat used in this apparatus is about 16″ long, is smoked on the inside, and is made of thin-walled clear quartz of 1″ I.D. and of semi-circular cross-section. A normal charge of zone refined Ge and seed is about 12 inches long and weighs about 500 gm. A photograph of the assembled apparatus appears in Fig. 10.

For the best results in crystal perfection and resistivity uniformity, the apparatus is run with the full length after-heater and at a slow pull
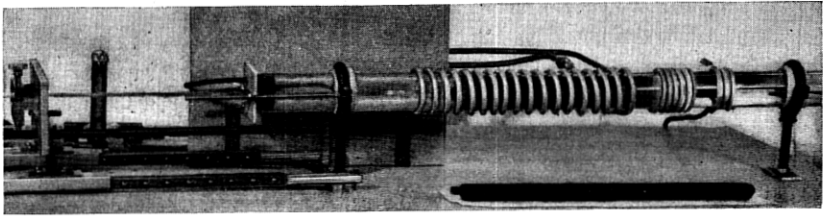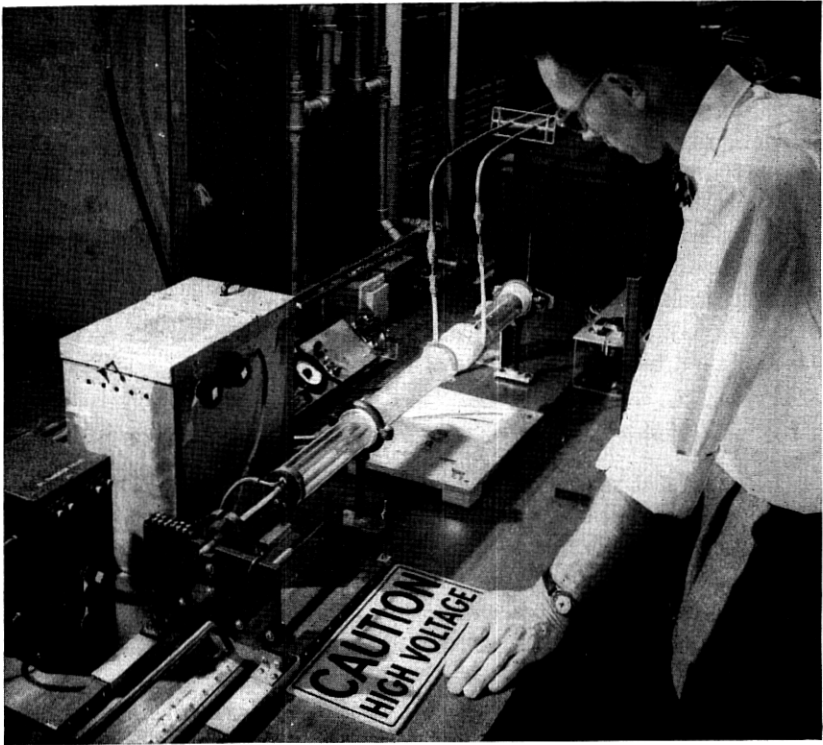
Fig. 10 — Zone leveler.

rate, 0.09 mils per second (approximately 1″ in three hours). For somewhat less critical demands a pull rate 10 times faster is used, with a shortened after-heater or none at all.

If it is desired to reproduce a resistivity obtained in the zone leveler, it is very convenient to reuse the solidified zone containing the impurity addition that yielded the desired resistivity. This solid zone, if undamaged (when cut from the finished ingot), will contain all of the solute that was not deposited during the ingot run. When it is remelted next to a seed the solute will redissolve into the liquid to yield very nearly
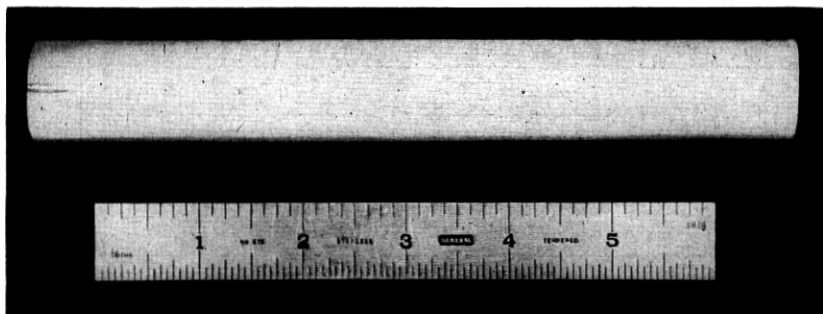
Fig. 11. — Photograph of zone leveled single crystal ingot.

the same C_L, provided that the zone volume is accurately reproduced. In this way it is readily possible to resume leveling as before and hence virtually to reproduce a desired resistivity. For the small k solutes, In and Sb, discussed in this paper the loss of C_L in one leveling run is so small as to be insignificant compared to other sources of error in this quantity.

PILOT PRODUCTION RESULTS

The capabilities of the zone leveling equipment and techniques just described may be evaluated with reasonably good accuracy on the basis of the measurement results obtained from more than 300 single crystal ingots so produced. Over 200 of these crystals were grown in the after-heater at the "slow" growth rate of 0.09 mils per second. The rest were grown with a short after-heater or none at all at a growth rate about ten times greater.

The ingots to be measured (see Fig. 11) were usually 4–6 inches long after removing seeds and solidified zones (i.e., 2–3 zone lengths), and were cut into 1 inch lengths. The ρ, τ, and ϵ measurements were taken on the flat ends of these segments. The results of the observations will be summarized and discussed in terms of the four device test requirements described earlier.

(1) *Compositional Uniformity*

The resistivity measurements were taken with a calibrated 4-point probe technique[16] at five locations on each ingot cross-section (center, top, bottom and each side). The spacing between adjacent points of the probe was 50 mils. Accordingly, these measurements would be insensitive to ρ fluctuations in the material of this order or smaller. However, an investigation by potential probing techniques, of Ge filaments cut from zone leveled ingots[17] indicates that ρ fluctuations in zone leveled material are

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[16] L. B. Valdes, Proc. I.R.E., **42**, p. 420, 1954.
[17] Erhart, D. L.. private communication.

TABLE I — AVERAGE RESISTIVITY VARIATIONS
(A) Along length axis. Grand Length Average ± 10%.

Growth Rate Mils per Second	n-Type		p-Type		Average ± %
	± %	No. of Ingots	± %	No. of Ingots	
0.9	9.9	27	10.9	33	10.4
0.8	7.6	12	17.4	16	13.2
0.09	9.0	108	9.3	137	9.2

(B) Over Cross-Section

Growth Rate Mils per Second	n-Type		p-Type		Average ± %
	± %	No. of Ingots	± %	No. of Ingots	
0.9	9.5	22	8.5	30	8.9
0.8	8.3	12	6.9	14	7.5
0.09	4.3	93	2.3	122	3.2

generally coarse — changing over distances 2 to 5 times larger in dimension than the 50 mil dimension in question. Thus the ρ data summarized here should give a reasonably valid representation of the true ρ variations in the ingots measured.

Table I summarizes the resistivity variations recorded as percentages of the mean resistivity of each ingot. These variations are separated into those observed (a) along the length axis and (b) over the cross-section, for the different growth conditions and resistivity types.

It is readily seen that the average variation along the length, about ±10 per cent, is larger than the average cross-sectional variation. The variations are not systematic along the length of the ingot and are chiefly due to fluctuation in the length of the liquid zone. An appreciable part of this variation is due to the effect, mentioned earlier, of discontinuities in the unmelted charges between 1 inch lengths of crystals that were being releveled. A smaller length variation of ρ, about ±7 per cent, was observed in those ingots grown from continuous charges.

Part B of the table shows that the variation of ρ over the cross-section is sensitive to the growth rate in the range covered. For slow growth, it is small, and one would reasonably expect that if further improvement in ρ variation were required, it should first be sought by improving the control of the zone length.

(2) *Macro Perfection*

Macro perfection of the pilot production product is extremely high. There were essentially no cases of polycrystallinity, or twinning, except
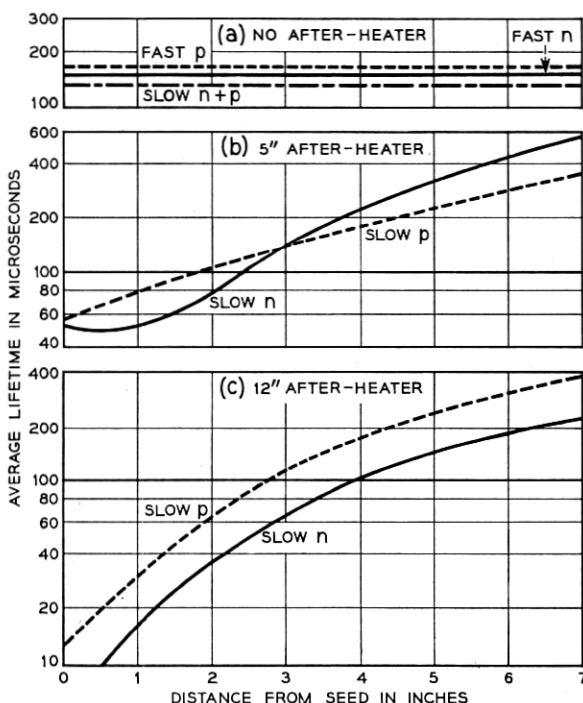
Fig. 12 — Average minority carrier lifetime plotted against distance from seed for 2–8 ohm cm crystals grown with 12″, 5″ and no after-heaters.

for clearly attributable causes such as power or equipment failure. There were few cases of lineage in the short after-heater and virtually none in the full after-heater, while lineage is not uncommon in ingots grown with no after-heater.

(3) *Micro Perfection*

Table II summarizes the etch pit density, ϵ, measurement results. In general, it can be seen that with the after-heater one can expect etch pit counts of the order of 1,500 pits per cm² which is lower than results without an after-heater by about an order of magnitude (and lower than

TABLE II — AVERAGE ETCH PIT DENSITIES, ε

	Growth Rate Mils per Second	ε Ave	σ	No. of Ingots
(12″ after-heater)	0.09	1560	770	39
(5″ after-heater)	0.09	3800	1600	3
	0.9	7000	1900	3
No after-heater	0.9	11000	6600	6

ϵ's of pulled Ge crystals by about two orders of magnitude). The lowest average count that has been observed is 40 pits per cm². This crystal was found to have the smallest X-Ray rocking-curve widths observed in germanium at Bell Telephone Laboratories — very nearly the theoretically ideal widths. The perfection indicated is exceptional — comparable to that of selected quartz crystals.

(4) *Lifetime of Minority Carriers*

τ data are summarized in Fig. 12 in which are plotted averages of the τ measurements on the ingot sections against distance from the seed. One sees a systematic rise in τ along the length axis of an ingot grown slowly in the after-heater. This is interpreted to indicate that the ingot is being slowly contaminated with chemical recombination centers during its long wait inside the after-heater at high temperatures. If improvement were needed in lifetime, it should be sought first by increasing the chemical cleanliness precautions, which were nonetheless strict in this work.

SUMMARY

A zone leveler has been developed to provide growth conditions suitable for the production of quality germanium single crystals. The crystals are nearly uniform and have exceptionally high lattice perfection. Similar levelers are in use in production.

The apparatus developed has been used to supply germanium single crystals for experiments and for the pilot production of a variety of point contact, alloy, and diffusion transistors. The machine operating at slow growth rate with an after-heater can produce one 6-inch 250-gm crystal per day. For less critical demands, it can produce several longer crystals per day.

Evaluation of the product indicates that resistivity variation on a cross-section of the ingot can be ±3 per cent and that along the length axis it can be controlled to ±7 per cent if a continuous charge is used. Furthermore, the crystals contain no grain boundaries or lineage and the scattered etch pit densities average about 1,500 per cm². Thus, the zone leveling process has proved to be simple, efficient, and capable of more than meeting the present specifications for quality germanium single crystals.