LB-1034

GROWTH OF SILICON CRYSTALS FOR TRANSISTOR APPLICATIONS

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LB-1034

1 OF 13 PAGES

JUNE 21, 1956

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Approved

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Growth of Silicon Crystals for Transistor Applications

Silicon single crystals have been grown by the Czochralski technique with electrical and structural properties suitable for transistor applications. This bulletin describes this technique and gives the growth conditions necessary for the best lifetime-to-resistivity ratio. The effects of other growth parameters are also considered.

Introduction

The Czochralski technique[1] of producing single crystals consists of withdrawing from the melt a single crystal seed which is rotated to maintain cylindrical geometry. It is apparent in this technique that the temperature gradient in both the melt and crystal, the rotational speed of the crystal, and the rate of withdrawal from the melt, all can be important in controlling the purity and the degree of crystalline perfection in the crystal. Although some of these experimental factors have been noted by several investigators[2,3] with respect to germanium, very little data exist with respect to silicon. Moreover, the observations on germanium are scattered and uncorrelated, and considerable disagreement exists among researchers as to the effect of these parameters on electrical properties. Thus, a program was instituted to investigate systematically the effect of the above factors on the electrical properties of resistivity and lifetime in silicon. An objective of this study was to obtain data on the experimental conditions which are best suited for the production of low resistivity (1 to 5 ohm-cm) silicon crystals of high carrier lifetime ($\geq 50\ \mu$sec).

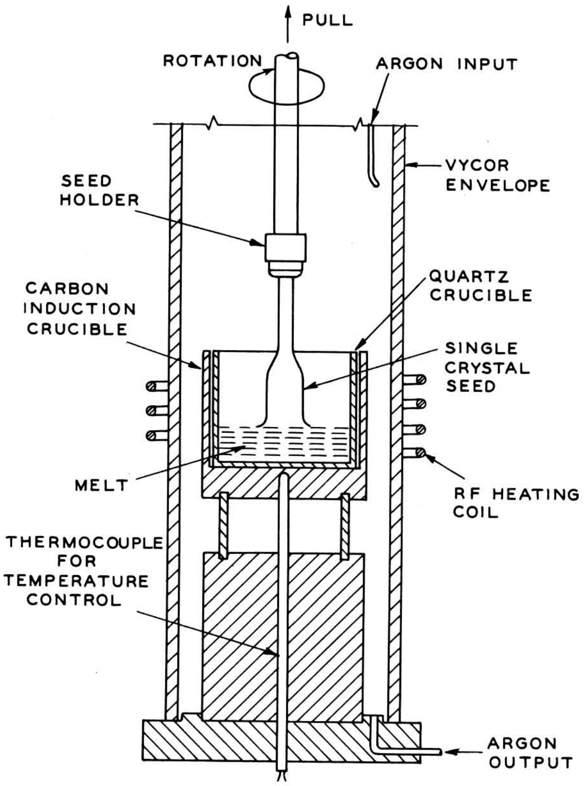


Fig. 1 – Schematic drawing of the crystal-growing apparatus for silicon.

Crystal Growth Technique

The apparatus used for growing single crystals by the Czochralski technique is shown schematically in Fig. 1. This apparatus is a product of several earlier designs, and its operation is quite simple. The molten silicon is contained in a high-purity quartz crucible which is supported by a carbon crucible. Radio-frequency power is fed to a surrounding coil, and currents induced in the carbon crucible provide the necessary temperature to melt the silicon. The temperature is measured and controlled by a thermocouple in contact with the bottom of the quartz crucible.

A transparent Vycor tube encloses the crucible assembly, and is made gas-tight by Silicone o-rings suitably placed in metal fixtures at its ends. Argon gas, which is purified by passing through titanium sponge at 850 degrees C and a dry-ice trap, enters the heating chamber through a quartz tube which makes contact with the wall of the Vycor tube approximately six inches above the quartz crucible. The flow of gas against the Vycor tube prevents SiO vapor from condensing on a portion of the Vycor tube. This is essential to maintain visibility of the crystal during crystal growth. The Si0 vapor is a product of the reaction between molten silicon and the quartz crucible.

A stainless steel shaft extending vertically into the heating chamber supports the single-crystal seed of silicon which touches the melt. Depending on thermal conditions in the melt and seed, the melt is maintained 15 to 40 degrees C above the freezing point of silicon. As the shaft is withdrawn, crystal growth occurs at the interface between the seed crystal and the melt, and a single crystal is produced. The shaft is also rotated during crystal growth to provide thermal symmetry in the melt and, hence, uniform geometry. The size of the crystal depends critically on the control temperature, withdrawal rate and, to a lesser extent, on the speed of rotation. This behavior results from the rate at which the energy of latent heat of fusion is released on solidification and its diffusion rate in the melt and growing crystal.

Before growing a single crystal, certain precautions must be taken to avoid contamination of the heating chamber. The quartz crucible, Vycor tube, and seed crystal are thoroughly cleaned with suitable chemical reagents, rinsed in distilled water, and then dried. The carbon induction crucible is of nuclear reactor graphite. and is baked at approximately 1600 degrees C in a vacuum. The silicon charge, obtained from DuPont in densified form, is placed directly into the cleaned quartz crucible. Final handling of equipment for assembly is done with glassine paper.

Electrical Measurement Techniques

The resistivity of the crystal and its conductivity type were determined by the four-point probe and thermal-probe techniques[4], respectively. In both measurements, the surface was cleaned by vapor blasting with alumina.

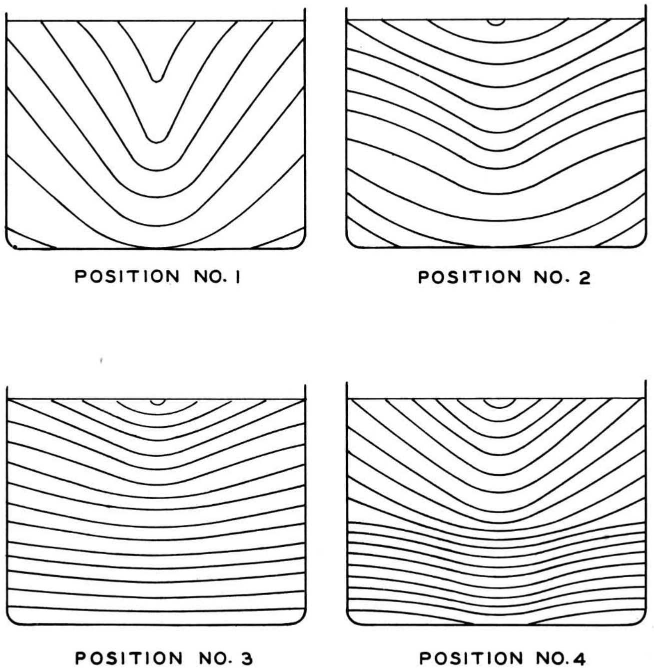
The pulse photo-conductivity method[5] was used to determine the carrier lifetime in the as-grown crystals. In this technique, the lifetime is obtained directly by measuring the time decay of excess conductivity after a pulse excitation of hole-electron pairs by a short flash of light. The conductivity variation is obtained from the voltage across a resistor in series with the sample and a bias battery. The specimens used in this measurement were in the form of sheets, 2 mm x 4 mm x 8 mm. The small surface-to-volume ratio eliminates any serious contribution due to surface conditions. Preparation of the specimens for measurement consisted of surface grinding and then mechanically polishing with No. 305 American-Optical compound. Electrical contacts were then made by first copper plating the ends, and then soldering with 63-percent-Pb – 37 percent Sn alloy. A final etch with standard CP-4 etch solution[6] removed the cold-worked layer from the mechanical treatment, and any surface film from the soldering process.

Effect of Temperature Gradient in the Melt and Crystal

For purposes of standardization, the same lot of DuPont silicon was used throughout this phase of the investigation. This starting material was n-type with a resistivity range of 5 to 13 ohm-cm in its single-crystal form. The rotational speed of the specimen and its rate of withdrawal was fixed at 50 rpm and 0.5 mm per min, respectively. In all cases, the axis of the seed crystal was coincident with a <111> direction.

Gradient in the Melt

The temperature gradient in the melt was varied by simply changing the position of the crucible in relation to the radio-frequency heating ring. In this manner, vertical differentials of 55 degrees, 105 degrees, 160 degrees, and 185 degrees C were obtained, with the bottom of the melt at the highest temperature. The nature of the thermal gradients at the four positions is best indicated by the isotherms in the drawings of Fig. 2. The isotherms


POSITION NO. 1

POSITION NO. 2

POSITION NO. 3

POSITION NO. 4

Fig. 2 – Nature of thermal gradient in melt for various positions of quartz crucible in relation to RF heating ring. Isotherms are constructed for changes of 10° C.

were constructed from data obtained by measuring the temperature across the melt at various depths by means of a Pt, Pt-13 percent Rh thermocouple protected by a thin quartz tube. It may be noted from Fig. 1 that, in addition to a vertical gradient, a radial one also exists. It is to be expected, however, that this gradient will be considerably decreased in magnitude by the rotation of the crystal during growth.

Fig. 3 shows the dependence of lifetime, τ, on the vertical temperature gradient in the melt, $(dT/dx)_L$. Each point on the curve represents an average of two tests. It may be seen that as $(dT/dx)_L$ increases, τ increases at a rapidly increasing rate from a mean value of 1 μsec for a 20 degree C cm^{-1} gradient to 10 μsec for a 69 degree C cm^{-1} gradient. Higher values of $(dT/dx)_L$ were not investigated due to increased difficulty in preventing freezing of the melt surface during crystal growth.

In connection with the results of Fig. 3, it is significant to note that the manner in which $(dT/dx)_L$ is increased could result in a decrease in the temperature of the solid in the vicinity of the solid-liquid interface.

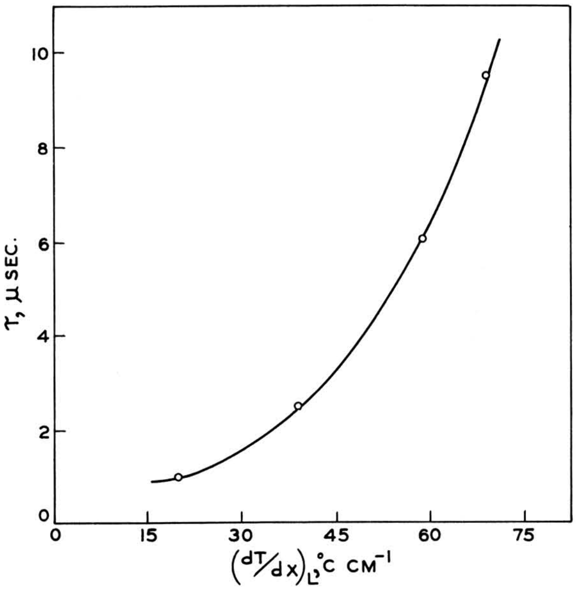


Fig. 3 – Dependence of lifetime, τ, in n-type silicon on temperature gradient $(dT/dx)_L$ in the melt.

Gradient in the Crystal

A temperature gradient in the solidifying crystal was obtained by directing a vertical jet of purified helium onto the end of the seed crystal, as shown schematically in Fig. 4 (The helium gas was purified by passing through an activated charcoal trap at -195 degrees C). The effect of this gradient during crystal growth was to raise the value of carrier lifetime from 10 μsec to 30-40 μsec. In one experiment, a carbon ring was placed on the quartz crucible to prevent, by deflection, the vertical jet of helium from reaching the solid-liquid interface. Under such conditions one would expect a sharp gradient of lifetime along the crystal, with the highest value near the seed end. The results of this experiment are shown in Fig. 5, from which it may be seen that the predictions were substantiated.

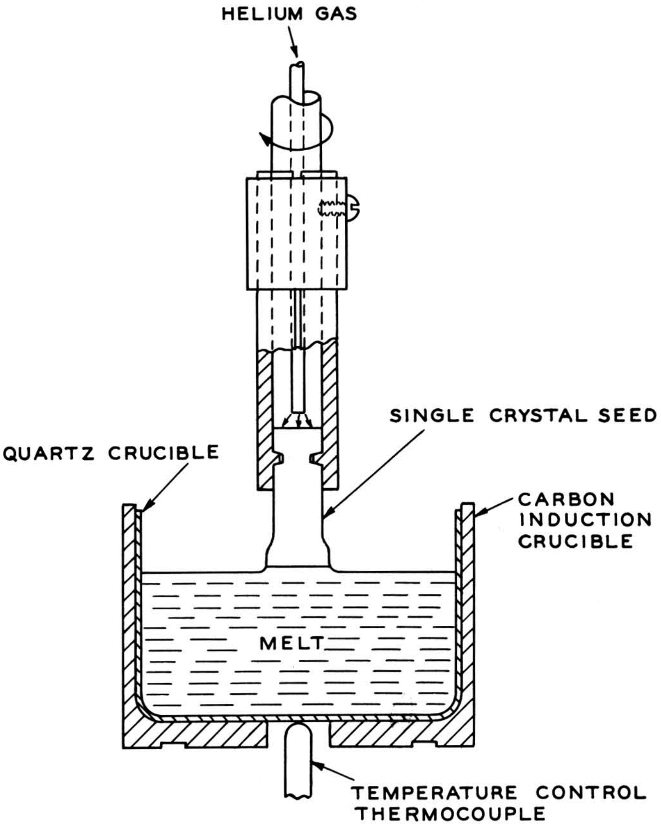


Fig. 4 – Schematic drawing showing manner in which helium gas jet was directed at seed end.

Fig. 6 shows the results of a second experiment in which the carbon ring was removed for the purpose of permitting the helium to reach the solid-liquid interface during crystal growth. It may be seen that although a gradient of lifetime still occurs along the specimen, the lifetime gradient is not as pronounced as in the crystal of Fig. 5. It is further interesting to note that, in the crystal of Fig. 6a, τ_3 is less than τ_4 despite the fact that τ_4 represents a portion of the crystal of lower purity. This apparent anomaly could be explained by supposing that the vertical helium jet could not effectively cool the portion of the crystal represented by τ_3, because of the outward growth of the crystal directly above it. Generally speaking, in all similar cases of shape changes during crystal growth the thin portion showed a drop of lifetime. This reasoning could also explain the higher value of τ_2 as compared to τ_1 in Fig. 6b, and the marked difference between τ_2 and τ_3 in both crystals of Fig. 6. This change

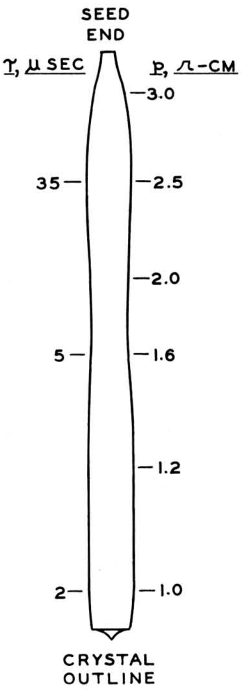


Fig. 5 – Variation of lifetime, τ, and resistivity, ρ, along n-type silicon crystal grown by Czochralski technique with helium gas jet directed at seed end and carbon ring on quartz crucible.

in lifetime of a crystal with changes in the gross geometry represents further evidence of the importance of a temperature gradient in the crystal on this electrical property.

To obtain a more uniform and effective temperature gradient along the entire crystal during growth, a jet of argon and then helium was directed on the growing crystal in the vicinity of the solid-liquid interface. With the argon-jet, lifetimes as high as 60-80 μsec were obtained, but a gradient of lifetime still occurred along the crystal. The helium jet, on the other hand, generally gave somewhat lower lifetimes, but the lifetime did not vary as much along the crystal. Typical results are shown in Fig. 7 a,b. Since helium is a better thermal conductor than argon, it would appear that there is a limit to the temperature gradient to be imposed on the crystal for best lifetime.

To examine this hypothesis further, a sharper thermal gradient was imposed on the seed by the use of a water-cooled seed holder along with the helium jet at the solid-liquid interface. Crystals grown under such conditions had still lower lifetimes, and an example is shown in Fig. 7c for comparison. Since the effect of water cooling the seed becomes increasingly less important with growth of the crystal, the bottom portion of the crystal in Fig. 7c was actually grown under thermal gradients similar to the crystal of Fig. 7b; yet its lifetime is appreciably lower. This would suggest that structural imperfections, once formed, can propagate along the crystal during growth in spite of variations in growth conditions.

Table I summarizes the data on the mean variation of carrier lifetime along the crystal with the temperature gradient in the crystal, $(dT/dx)_S$. It may be seen that a thermal gradient of approximately 250 degrees - 300 degrees C per cm is necessary for maximum lifetime under the prescribed conditions of growth. The thermal gradient in the seed crystal was determined by a thermocouple in contact with the seed approximately 2 cm above the melt surface.

The effect of a thermal gradient in the growing crystal on its resistivity range is also shown by the data in Table I. It may be seen that an increase in the thermal gradient by the use of gas jets directed at the growing crystal in the vicinity of the solid-liquid interface results in a decrease in the resistivity range from 3-10 ohm-cm to 0.8-6 ohm-cm. This effect strongly suggests that the decrease in resistivity on varying the position of the radio-frequency coil with respect to the melt (described in the preceding section) was due to an increase of the thermal gradient in the crystal, and not in the melt. It is further significant to note that although the highest average lifetime (70 μsec) is obtained by using the argon gas jet, the τ/ρ ratio is better along the crystal with the helium jet as a result of the resistivity change with thermal gradient.

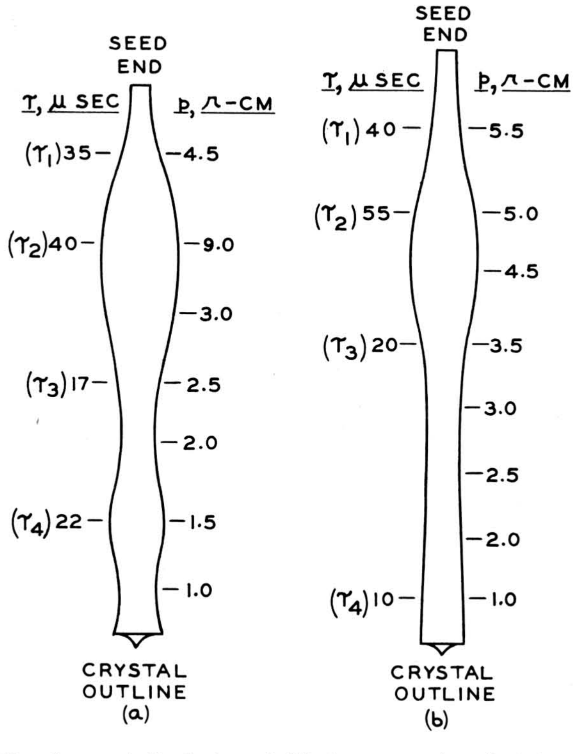


Fig. 6 – a, b-Variation of lifetime, τ, and resistivity, ρ, along n-type silicon crystals grown by Czochralski technique with helium gas jet directed at seed end.

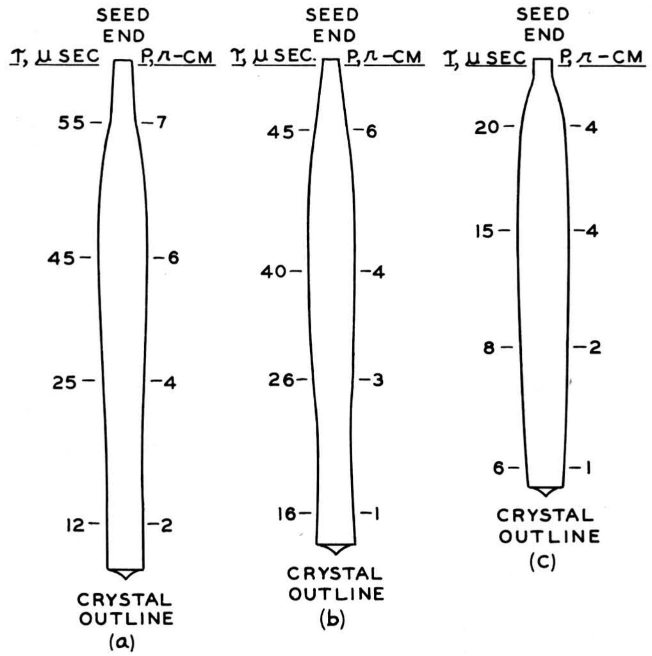


Fig. 7 – (a,b,c) Effect of increasing thermal gradient in crystal on lifetime in silicon: (a) –argon gas jet, (b) –helium gas jet, (c) –helium gas jet and water cooled seed holder.

Table I. Effect of thermal gradient in crystal on lifetime and resistivity ranges in n-type silicon.

No. of crystals	$(dT/dx)_S$, °C cm^{-1} (approximate)	τ, μ sec	ρ, ohm-cm	τ / ρ
2	100	2 - 10	3 - 10	0.7 - 1
3	250	12 - 70	1 - 8	12 - 9
3	325	14 - 50	0.8 - 6	18 - 9
2	425	5 - 25	0.7 - 5	7 - 5

Effect of Growth Rate

Du Pont silicon, Lot. No. 101A, was used for this phase of the investigation. This material gave p-type single crystals with a resistivity range of 25 to 55 ohm-cm. The crystals were grown with a <111> longitudinal axis, a rotational speed of 50 rpm, a temperature differential of 185 degrees C in the melt (crucible position No. 4), and a helium jet directed in the vicinity of the solid-liquid interface. Growth rates ranging from 0.1 mm per min to 2.5 mm per min were studied, and the results are summarized in Table II. In the columns are listed the number of specimens, the rate of growth, dx/dt, the mean range of lifetime, (τ), and resistivity, (ρ), along the crystal, and the corresponding τ / ρ values.

Table II. Effect of growth velocity on lifetime and resistivity along p-type silicon crystals.

No. of crystals	dx/dt, mm min^{-1}	τ, μ sec	ρ, ohm-cm	τ / ρ
1	0.1	30 - 65	34 - 50	0.9-1.3
3	0.5	34 - 70	30 - 48	1.1-1.5
2	1.0	17 - 35	25 - 45	0.7-0.8
2	2.5	6 - 18	18 - 44	0.3-0.4

From the results, there appears to be an effect of growth velocity on both lifetime and resistivity. The lifetime decreases appreciably for growth rates above 0.5 mm per min.; whereas the resistivity decreases slowly, but continuously with increasing growth velocity. The resistivity effect appears to be more marked for the lower value in the range; i.e., for the last portion of the crystal to solidify. It is significant to note that at this stage of growth the helium jet is not directly above the solid-liquid interface; and hence, the temperature gradient in the crystal is not as sharp. Hence, any effect of growth velocity on the temperature gradient in the crystal would be more pronounced at this later stage of growth. Since the resistivity is only slightly affected by changes in the growth velocity, the value of τ / ρ varies in the same manner as the lifetime.

Several experiments were carried out in which the growth rate was varied during the growth of the crystal. In one experiment, the first half of the specimen was grown at 0.5 mm per min, while the remainder was grown at 2 mm per min. In another, the conditions were reversed; i.e., the growth velocity was changed from 2 to 0.5 mm per min. In both cases, and in other similar ones, it was generally found that the effect of the initial growth velocity on lifetime continued well into the portion of the crystal grown at the other rate. This effect is further evidence in support of the idea that imperfections, once formed, continue to propagate along the crystal despite changes in conditions of growth.

Effect of Rotational Speed

For this phase of the investigation, the starting material (Du Pont Lot No. 119A) yielded p-type single crystals with a resistivity range of 4 to 18 ohm-cm. The crystals were grown along a <111> direction at a fixed growth velocity of 0.5 mm per min. A helium jet was directed in the vicinity of the solid-liquid interface, and the crucible was in position No. 4 (see Fig. 2) with respect to the radio-frequency heating ring. The effect of rotational speed was studied in the range, 0 - 150 rpm; and the results are given in Table III. Listed are the number of crystals examined at the various speeds of rotation (R), the ranges of both lifetime (τ) and resistivity (ρ) along the crystal, and the values of the lifetime-to-resistivity ratio (τ/ρ).

Table III. Effect of rotational speed on lifetime and resistivity along p-type silicon crystals.

No. of crystals	R, rpm	τ, μ sec	ρ, ohm-cm	$\frac{\tau}{\rho}$
2	0	2 - 6	1 - 6	2 - 1
2	5	3 - 8	2 - 8	1.5 - 1
3	50	4 - 8	5 - 16	0.8 - 0.5
1	150	3 - 6	8 - 25	0.4 - 0.2

It is apparent from the results that the resistivity increases significantly with increasing speed of rotation, whereas the lifetime is relatively unaffected. Thus, the ratio of lifetime-to-resistivity increases with decreasing speed of rotation.

The effect of varying the rotational speed during growth was studied in several specimens. A typical result is shown in Fig. 8, where the top half of the crystal was grown at a rotational speed of 5 rpm and the remainder at 150 rpm. It may be seen that the resistivity, instead of continuously decreasing with growth of the crystal in the normal way, increases when the rotational speed is raised to 150 rpm. This is to be expected from the data in Table III. Again, the lifetime shows no significant dependence on variations in speed of rotation.

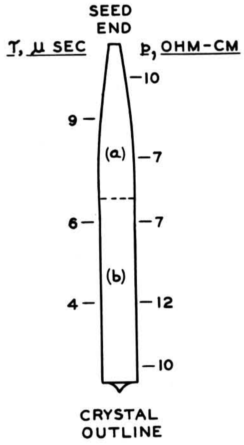


Fig. 8 – Effect of variable rotational speed on lifetime and resistivity along p-type silicon crystal (a) 5 rpm (b) 150 rpm.

Effect of Impurity Additions

Single crystals were grown in the resistivity range of 1 to 10 ohm-cm with antimony, arsenic, bismuth, and selenium as n-type impurities, and aluminum, boron, and indium as p-type impurities. The antimony, arsenic, bismuth, and boron additions were made in the form of master alloys with silicon; whereas, the aluminum and indium were added directly. The selenium, because of its relatively low boiling point, was added as the compound, PbSe, which has a melting point of approximately 1088 degrees C. This compound is particularly desirable since the tetravalent lead does not contribute to the resistivity.

By using the most suitable arrangements for crystal growth, as determined from the foregoing experiments, lifetime-to-resistivity ratios of from 3 to 20 were obtained for the n-type material. For the p-type material the ratio was generally 1, although on a few occasions 3-4 was obtained.

Since p-type material was of great interest, most of the effort on the impurity effect was concerned with additions of aluminum, boron, and indium. Boron has advantages in that it has a distribution coefficient of approximately unity, which results in a uniform resistivity along the crystal; and it diffuses substitutionally in silicon[7], which suggests that it is not a "lifetime-killer".

Fig. 9 shows the effect of boron additions (plotted as resistivity) on carrier lifetime in crystals grown under similar conditions. It may be seen that the lifetime decreases at a slightly decreasing rate with increasing boron content over the resistivity range, 2-80 ohm-cm, with lifetime-to-resistivity ratios ranging from 1-2. Unfortunately, no theoretical significance can be attached to the curve of Fig. 9, since there are too many recombination centers in the crystal for proper mathematical treatment. Aside from the usual structural imperfections (vacancies, interstitials, and dislocations), there are also chemical impurities (from spectrographic analysis: Cu, B, Zn, and Fe) which can act as recombination centers. Thus, the data in Fig. 9 has, at best, only empirical significance.

Since primary structural imperfections can have a pronounced effect on lowering the lifetime of charge carriers by catalyzing their recombination, several experiments were made in which lead and germanium were added to silicon in an attempt to lower the density and/or effectiveness of certain imperfections without affecting the resistivity. The lead, because of its apparent immiscibility in solid silicon, was expected to appear as precipitated particles which would nucleate the condensation of vacancies, thereby reducing their density. If a slight solid solubility did exist, then the lead would migrate to dislocations, and reduce the stress field around them. The germanium, on the other hand, because of its complete solid miscibility with silicon, could preferentially migrate toward regions of low angle boundaries (e.g., mosaics, lineage), and reduce their relative energy. The occurrence of any one of the above mechanisms would contribute towards raising the lifetime of the crystal. From the data in Table IV, it may be concluded that for the proportions used, lead can raise the lifetime in silicon, whereas germanium has a negligible effect.

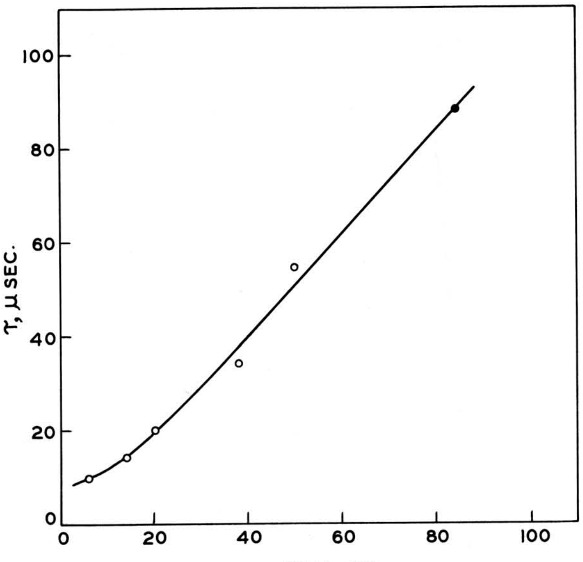


Fig. 9 – Effect of resistivity on carrier lifetime in p-type silicon: ● = undoped, o = boron doped.

Table IV. Effect of small additions of lead and germanium on lifetime in silicon.

Impurity	Content At. percent	τ, μ sec	ρ, ohm-cm	Type
--	--	8	4	n
Pb	0.01	17	3	n
--	--	5	7	p
Pb	0.01	10	7	p
--	--	7	10	p
Ge	0.01	6	9	p
Ge	0.10	7	11	p
Ge	1.0	9	10	p

Metallographic Examination

Metallographic studies of edge dislocations were made on a number of crystals which gave lifetime-to-resistivity ratios suitable for transistor applications. The average dislocation density in these crystals ranged from 10^3 to 10^4 cm^{-2}. The etchant used to bring out the edge dislocations was a mixture of 3 parts No. 4 etch and 5 parts No. 1 etch[6]. The photomicrographs in Fig. 10 show the typical appearance of edge dislocations in silicon on a <111> plane. Although no detailed study has been made, as yet, on the variation in dislocation density with changes in growth conditions, crystals have been grown

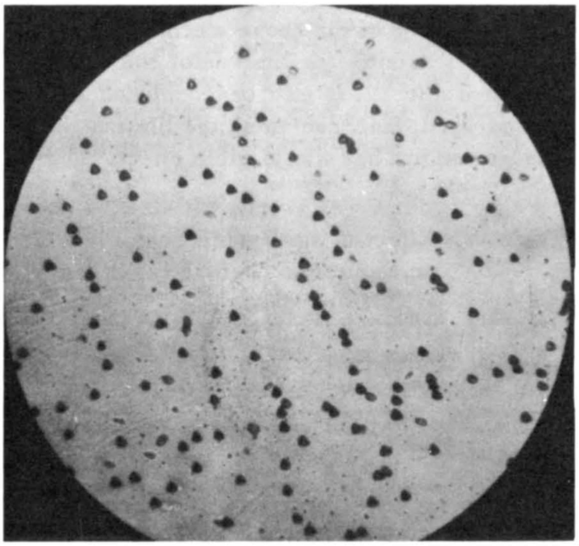


Fig. 10a – Appearance of edge-type dislocation pits in silicon at low magnification. x75.

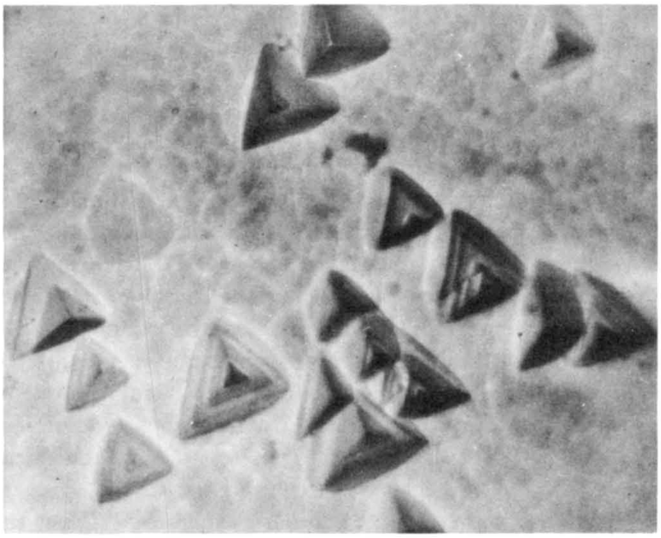


Fig. 10b – Appearance of edge-type dislocation pits in silicon at high magnification. 250x.

with essentially no edge-dislocations. This was made possible by preventing the occurrence of slip during growth, which is believed to be the main source of dislocations. An example of octahedral slip, as a result of a non-uniform temperature distribution across the crystal, is shown in Fig. 11.

Several crystals were examined along their <111> axes for birefringence in infra-red apparatus. These crystals showed no evidence of birefringence which indicates that, if heterogeneous strains do exist in the crystal, the strains are too small to be observed by the present apparatus. This is in contrast to the distinct birefringence pattern observed in silicon crystals grown at General Electric, and reported by Dash[8] using a similar apparatus. In this connection, it is interesting to note that a thermal conversion at 200 degrees C from p-type to n-type is obtained in the G.E. crystals exhibiting birefringence. In our crystals this conversion does not occur. This could be attributed to the apparent absence of large strain inhomogeneities which could greatly accelerate diffusion processes responsible for precipitation or dissolution phenomena. The absence of this low temperature conversion is essential to device fabrication using p-type material.

Purification Experiments

For transistor devices using p-type material it is desirable to obtain lifetime-to-resistivity ratios of 4-5, and an edge dislocation density of less than 10^4 cm^{-2}. It is apparent from the foregoing that the crystals have a sufficiently low dislocation density (10^3 - 10^4 cm^{-2}); but the lifetime-to-resistivity ratio, which is near unity in the resistivity range 2-5 ohm-cm, is too low. In an attempt to increase this ratio by improving the lifetime, purification by multiple-pulling was undertaken, using the best known arrangements for crystal growth. In this technique, which is analogous to zone-refining[9], the crystal is pulled several times; and for each pull there is left in the crucible a small amount of liquid which contains the major portion of impurities with distribution coefficients considerably less than unity. This liquid residue, which is discarded, avoids the excessive handling and possible contamination encountered in cutting the last portion of the crystal to solidify.

The boron was added to the initial melt so as to purify it along with the silicon during the multiple pulling. Since the distribution coefficient of boron in silicon is near unity, the resistivity of the crystal does not change significantly with number of pulls.

Table V gives the data pertinent for evaluating six crystals grown by this method of purification. It is at once apparent that the lifetime-to-resistivity ratios are in the range, 3-5; and the edge dislocation density varies from 10^3 - 10^4 cm^{-2}. This material, therefore, meets with the specifications required for transistor devices.

For better control of both resistivity and carrier lifetime on doping, the as-received needle-form of Du Pont silicon is now purified by horizontal zoning in thin fused-silica boats (0.007 to 0.010 inch wall thickness). Direct rf induction heaters are used, and preheating to 1000 degrees C is done in a nichrome-wound furnace in series with the heaters. Six zone passes yield p-type material

Table V. Effect of purification by multiple pulling on lifetime and resistivity in boron-doped silicon crystals.

Crystal No.	Crystal Axis	No. of Pulls	τ, μ sec	ρ, ohm-cm	$\frac{\tau}{\rho}$	Dislocation Density, cm^{-2}
392	<111>	5	12 - 17	2.5-3.5	5	1000
414	<111>	5	12	1.5	8	4000
436	<111>	5	6 - 15	3.5-4.0	2 - 4	6000
454	<111>	4	10 - 15	2.7-3.1	4 - 5	3000
452	<111>	4	8 - 15	2.5-3.0	3 - 5	6000
C-55	<111>	3	10 - 20	3.2-4.1	3 - 5	2000

with a resistivity of 200 to 300 ohm-cm. The uniformity in resistivity along the ingot suggests that the major impurity is boron.

In view of its reactivity with molten silicon, the quartz crucible used in growing single crystals can represent a serious source of chemical contamination. To avoid this, attempts were made to melt silicon in other materials. Crucibles of aluminum oxide, various mixtures of carbon and graphite, soot-coated quartz and, most recently, carbon coated with silicon carbide (Norton Co. Rokide "C" coating) were tried, but with no success. Thus, it appears that, at present, one is confined to the use of fused quartz as a crucible material. The presently available high-purity variety has done much to curtail the seriousness of this limitation. Moreover, on melting the silicon charge, care is taken to avoid excessive superheating, so as to keep the reaction rate of molten silicon with the quartz crucible to a minimum.

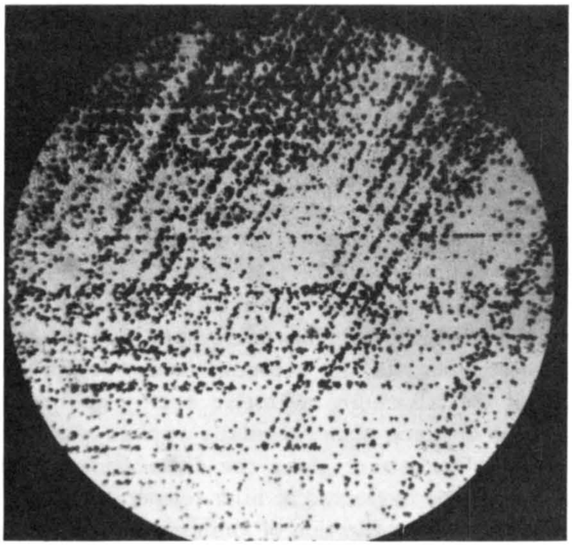


Fig. 11a – Appearance of octahedral slip on two systems in a silicon crystal produced by the Czochralski technique. Plane of observation is a (111). x30.

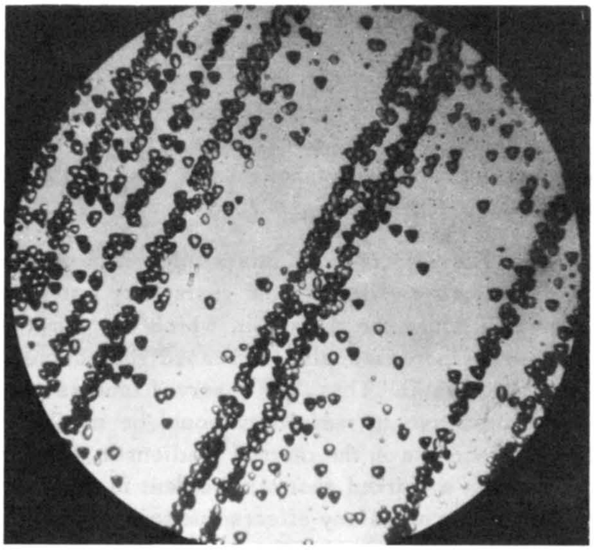


Fig. 11b – Appearance of octahedral slip in silicon crystal, as a result of non-uniform thermal conditions during growth, at higher magnification. x 100.

Summary of Observations

Silicon single crystals have been produced by the Czochralski technique with electrical and structural properties suitable for transistor applications. The principle observations responsible for these properties are summarized below, and a brief discussion is included for completeness.

1. It has been shown that the most suitable crystal growth conditions for obtaining the best lifetime-to-resistivity ratio are:

(1) a temperature gradient in the liquid of $\approx$ 70 degrees cm^{-1}

(2) a temperature gradient in the crystal of $\approx$ 300 degrees C cm^{-1}

(3) a growth velocity of 0.5 mm min^{-1}

(4) a rotational speed of 10 rpm

Ratios of 1-3 for p-type and 5-20 for n-type material were obtained in the resistivity range, 1-10 ohm-cm.

2. The most significant changes in carrier lifetime were brought about by varying the thermal gradient in the crystal, which also affected the resistivity. The τ/ρ ratio increases markedly with increasing $(dT/dx)_S$, reaching a maximum value for a gradient of 300 degrees C cm^{-1}. At higher gradients, the lifetime begins to decrease significantly.

3. The resistivity increases appreciably with the speed of crystal rotation in the range, 0-150 rpm; whereas the carrier lifetime is relatively unaffected. Thus, higher lifetime-to-resistivity ratios are obtained by decreasing the speed of rotation.

4. Variation in the rate of crystal growth from 0.1 to 2.5 mm min^{-1} affected lifetime and resistivity in a similar manner. From 0.1 to 0.5 mm min^{-1} there was little effect, but for velocities above 1 mm min^{-1} both properties showed a decrease.

5. The effect of an increasing temperature gradient in the melt on lifetime and resistivity was difficult to ascertain, since the manner in which the temperature gradient was increased also increased the thermal gradient in the crystal. Thus, the observed increase in lifetime and decrease in resistivity could be attributed as well to an increase in the thermal gradient in the crystal. Nevertheless, a marked thermal gradient in the melt can be expected to curtail any effects due to supercooling.

6. Zone purification of p-type material (boron-doped) by multiple pulling resulted in an increase in the average lifetime-to-resistivity ratio from 1 to 4.

7. The edge-dislocation density in p-type crystals with suitable lifetime-to-resistivity ratios ranged from 10^3 - 10^4 cm^{-2}. Polarized infra-red examination revealed the absence of localized strains of large magnitude.

It is apparent from the above results on resistivity that the effective solubility and, hence, distribution coefficient of an impurity depends on the thermal gradient in the crystal, as well as on the rotational speed. Regardless of whether the thermal gradient was increased by using gas jets, increasing the growth rate, or raising the position of the crucible relative to the heating unit, more impurities were incorporated in the solid with greater thermal gradient in the crystal. Thus, the relatively small effect of growth velocity on resistivity could be attributed to the presence of a large thermal gradient in the crystal as a result of the use of a helium gas jet. This would also explain the greater changes in resistivity with growth rate in the last portion of the crystal to solidify (see Table II), where the effect of the gas jet on the thermal gradient is considerably reduced because of its positioning. It would appear, therefore, that the resistivity gradient usually obtained along the crystal could be counteracted by a controlled variation of the thermal gradient in the crystal during growth.

The effect of increased rotational speed on resistivity is probably due to a decreased tendency towards constitutional supercooling, which results from an excess impurity concentration in the liquid at the solid-liquid interface. Variations in the rotational speed would be expected to greatly influence the rate of diffusion of these impurities into the bulk of the melt, thereby affecting the probability of trapping the impurities in the crystal during growth. This is probably reflected in the more uniform resistivity across the crystal with moderate speeds of rotation.

It is difficult at this time to speculate on the variation in carrier lifetime with temperature gradient in the crystal, since the results are not sufficiently definitive to determine the role of primary structural imperfections as recombination centers. It is evident, however, from the metallographic studies that in any analysis of this type one must at least take into account dislocation densities of 10^3 to 10^4 cm^{-2} as a result of octahedral slip during crystal growth. The energy per unit length of a dislocation consists of a potential energy due to the distortion of the lattice and a kinetic energy due to its motion. In the absence of an externally applied shear stress, the thermal component gives the dislocation a mobility which cannot be neglected at high temperatures. This is manifested in the migration of dislocations to form small angle boundaries (lineage), which are known to be deleterious to carrier lifetime. Since the mobility of the dislocation decreases very rapidly with temperature, it can be strongly affected by variations in the thermal gradient of the crystal during growth. Thus, the higher lifetime obtained with increased thermal gradient could be attributed to the decrease in the mobility of the dislocations and the lineage structure.

Since silicon crystals grown from the melt can be expected from thermodynamic considerations to contain a high concentration ($\approx 10^{17}$ cc^{-1}) of vacancies at the melting point, one must also consider the possibility of the existence at room temperature of vacancies well in excess of their equilibrium concentration. The low self-diffusion coefficient for silicon (10^{-12} cm^2 sec^{-1} near the melting point), would require abnormally long times for the vacancies to escape by migration to the surface, and the edge-dislocation density is insufficiently high for their complete removal by a condensation process. Thus, on cooling silicon crystals from the freezing point one can expect either a supersaturated solid solution of vacancies, or an aggregation of vacancies into discs, as is often encountered in precipitation phenomena from a metastable solution. With continued condensation of vacancies these discs can grow to a critical size, at which point the lattice across the disc will collapse to form general dislocation rings. This mechanism of producing dislocations was first proposed by Seitz[10] to account for the observed dislocation densities in crystals which were carefully grown from the melt.

It is apparent that the occurrence and density of the above defects will depend upon the temperature and the time at any given temperature for vacancy diffusion to occur. Thus, the magnitude of the temperature gradient in the growing crystal will govern the manner in which the vacancies will condense, as well as govern the size of the discs and their subsequent collapse into dislocations. The presence of a sharp thermal gradient (300 degrees C cm^{-1}), which yielded the highest values of lifetime, would be expected to retard the agglomeration of vacancies into discs.

It is noteworthy that the same value of lifetime was obtained in crystals of similar resistivity but markedly different dislocation density. This would indicate that there is no simple correlation between carrier lifetime and dislocation density. Instead it suggests some form of point defect interaction with dislocations such as vacancies and interstitial impurity atoms of a concentration $< 10^{13}$ cc^{-1}.

To conclude, the presently available data on silicon is not complete enough to propose a mechanism which would account for the observed variations in carrier lifetime with crystal-growth parameters.

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