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RESISTIVITY STRIATIONS IN SINGLE-CRYSTAL GERMANIUM

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Approved

Stuart Wm. Seeley

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Introduction

The detection and elimination of local resistivity variations in single-crystal n-type germanium is important in the preparation of material for making transistors of uniform characteristics. These variations, or striations, may occur during crystal growth and can be of a quasi-periodic nature. They are not in evidence as a disturbance of the single-crystal structure, which may be entirely satisfactory even in badly striated samples. Under some growing conditions, such as very slow rotation of the seed crystal during growth, the variations of resistivity can be as much as 2:1 in adjacent parts of the crystal. Detection of pronounced striations is possible by a potential micro-scan of a polished crystal bar through which a current is passed. However, this bulletin describes a new and much more sensitive method in which the polished crystal is pulse plated with a light coating of copper which makes the striations visible, even when they are very small in magnitude.

Correlation between resistivity variation and the external geometry of the grown crystal has been found. Severe resistivity variations can be avoided by perfecting the uniformity of growing conditions or by rapidly rotating the growing crystal with or without agitation of the melt. It has also been found possible to reduce the magnitude of striations by annealing at a high temperature, although the sensitivity of the copper-plating test is sufficient to show residual striations even in samples which have been annealed for a week. The discussion given here applies specifically to crystals grown by the Czochralski technique as described in LB-892, *Preparation of Single Crystals of Germanium and Silicon*. However, much of the discussion is equally applicable to crystals grown by other methods.

General Discussion

When single crystals of germanium are grown by the method described in LB-892 there is ordinarily some segregation of impurities. This results in a slow variation of resistivity along the length of the crystal. As shown in LB-885, *Electrical Measurements on Germanium*, this variation can be measured by passing a current through the crystal and measuring the potential distribution along its length by means of a probe and a high-impedance voltmeter.

This bulletin covers an investigation of a much more rapid variation in the resistivity of the crystal which may occur during crystal growth and is sometimes superimposed upon the slower variation. This rapid variation results from an undesirable inhomogeneity in the impurity distribution and is not necessarily accompanied by any other obvious electrical or physical defect. It is a possible cause of trouble in obtaining uniform transistors. The work on which this bulletin is based indicates that the most serious inhomogeneities are caused by rotating the crystals too slowly as they are being grown.

These variations are usually of too short range to be detected by the method described above. However, by probing short bars with polished faces and using currents of the order of 100 ma, a potential micro-scan may be made which will reveal the more obvious striations. A highly sensitive technique for detecting these striations has now been developed.

Occurrence of Striations

Large local variations of impurity concentration in single-crystal germanium have previously been reported by Burton and by English[1]. Two methods of revealing these variations were used. English melted a low-melting-point alloy on the surface of the germanium and then removed it with an acid etch thereby revealing the fluctuations. He reported that annealing did not remove them. In independent work, Burton showed similar striations by a radioactive autograph method and found, in addition, that the resistivity and lifetime vary with these fluctuations. More recently Chalmers has reported similar effects in lead-bismuth alloys[2]. Variations of resistivity of the same kind have been detected at RCA Laboratories by a different method.

The germanium here considered is single-crystal material grown by withdrawing a seed crystal from a pot of molten germanium. The plane of the variation of impurity concentration, if it occurs, is the plane of the growing interface, successive planes varying in resistivity. Thus the crystal is made up of alternate layers of high and low resistivity materials. The magnitude and spacing of these variations depend on the growing conditions. Variations of resistivity of as much as 2.2 to 1 have been detected in successive laminae under certain conditions whereas, under other other growing conditions, little or no striation is found.

Detection of Striations

Resistivity variations can be measured by passing current through a polished bar of uniform cross-section and mechanically scanning the surface with a fine point whose potential is measured. This method is straightforward but slow. Its sensitivity is greatly limited by random and unavoidable fluctuations in the mechanical system.

A much more sensitive and effective technique for revealing resistivity striations makes use of plating the germanium with copper, so as to make the striations visible. The crystal is cut in the form of a rod, bar, or plate with the long dimension parallel to the direction of growth. It is then ground, polished, and immersed in an acid copper-sulphate solution. Pulses of fairly high voltage are applied to the sample and the resulting current causes copper to plate preferentially on the low resistivity portions of the crystal. Maximum visual contrast may be obtained by suitably adjusting the resistivity of the electrolyte, the magnitude and duration of the pulses, and the pulse repetition rate. The purpose of pulsing is to allow diffusion to replace the ions lost in the immediate vicinity of the rapidly plating region thereby restoring the uniformity of the resistivity of the electrolyte.

A system which has been found useful is a 1-μf condenser which is alternately charged from a 300-volt supply and discharged through the plating solution. A motor-operated switch provides a repetition rate of from ½ to 3 pulses per second. A plating time of from 1 to 5 minutes has been found adequate for most samples. The resistivity of the electrolyte is best adjusted to the sample being analyzed, and is of the same order of resistivity. Solutio

[1] Conference on Electron Devices, University of New Hampshire, June 21-22, 1951.

[2] M. T. Stewart, R. Thomas, K. Wavehope, W. C. Winegard and B. Chalmers, "New Segregation Phenomena in Metals", *Phys. Rev.*, Vol. 83, p. 657; August 1, 1951.

resistivities in the range of 3 to 30 ohm-cm have been found useful.

Almost invariably, there is associated with these abrupt changes in resistivity some change in the surface structure of the crystal. Frequently this is of the nature of slight changes in diameter of the crystal. However, surface irregularities do not always have their counterpart in large resistivity variations.

Cause of Striations

The striations are believed to result from changes in the rate of advance of the growing interface. When the rate is slow, the impurities rejected by the solid are largely disbursed throughout the melt by diffusion and mixing. When the rate is fast, however, a bow wave of impurities forms at the growing interface. This results in an artifically high concentration of impurities in the melt which the interface sees and a consequent increase in the impurity accepted by the solid. The rate of advance of the growing interface may be changed by a number of means. The possibilities of cyclic change are particularly interesting since, very often, the striations have a cyclic character. Such periodic changes may be artifically produced by cycling the temperature or pulling speed or they may occur spontaneously due to some mechanical instability. One such possibility is that the meniscus is unstable; the melt is pulled up by the growing crystal until a critical position is reached and then drops back a little. This has the effect of a varying pulling speed although the external pulling speed is constant; the phenomenon has actually been observed. Another possibility is that there may be a thermal instability in the growing process due to an unstable balance between heat of fusion and conduction of heat away from the interface. Thus under certain growing conditions, the system may be inherently unstable and the rate of growth may oscillate.

By far the most pronounced striations observed have resulted from a slow rotation of the crystal as it was growing. Presumably this is due to a non-uniform temperature distribution in the melt resulting in faster growth in one portion of the pot than in another. If the crystal is not rotated, this results merely in a tilting or shaping of the growing interface which restores a constant rate to the whole interface. If the crystal is rotated, however, the result is two or more concentric spirals of material of different resistivity.

Suggested Means of Avoiding or Eliminating Striations

When the cause of the striations is known, a cure can be devised. To prevent striations resulting from the temperature variations of the melt, good furnace temperature control is required. It is estimated that the temperature of the melt must be constant within $\pm \frac{1}{2}$ degree C. To eliminate striations due to variations in the pulling speed, resulting from bad gearing etc., smooth pulling is necessary. It may be desirable, however, to superimpose on the smooth rate a high-frequency vibration to eliminate the meniscus instability. This can be done if the frequency is too high to appreciably affect the growing interface. If the striations result from an inherent thermal instability, the proper operating conditions (pulling speed, temperature and temperature gradient) may be found to minimize the instability.

When the striations are introduced by rotation, there are several possible cures. Many cold spots may be created in the furnace and cause a structure so fine as to be harmless. The speed of rotation may be increased so that the period of the striations is very small. There is good reason to believe that, as the period is made smaller, the amplitude is also made smaller. Thus a rotation of one revolution per mm of crystal growth may introduce serious striations when a rotation of ten revolutions per mm of crystal growth will yield homogenous material. The temperature of the melt may be made much more uniform (as, for example, by a heat-distributing shield) thereby decreasing the difference in resistivity between the concentric spirals. The melt may be vigorously agitated to destroy the effect of any cold spots and to reduce the bow wave of impurities. Crystals have been grown with high-speed rotation and/or vigorous agitation of the melt which indicate that both these processes are successful in greatly reducing striations.

A word of caution is necessary. When the speed of rotation is increased or when the melt is agitated, stable flow patterns may be produced which result in one portion of the crystal being permanently in a region of higher flow rate than another. Thus one portion of the growing crystal (for example, the region near the center of a rotating crystal) may be confronted by a melt richer in impurity than that facing another. This results not in periodic variations of resistivity along the crystal but rather in variation across the crystal. Therefore care must be taken to insure either very uniform or quite random circulation of the melt.

Annealing

It has been found that the proper annealing treatment reduces the amplitude of the resistivity striations, although there are no tests so far which show their complete elimination by annealing alone. It should be emphasized furthermore that, if homogeneous crystals are desired, it is better to grow unstriated crystals than to try to reduce the striations once they appear. Not only does this mean fewer

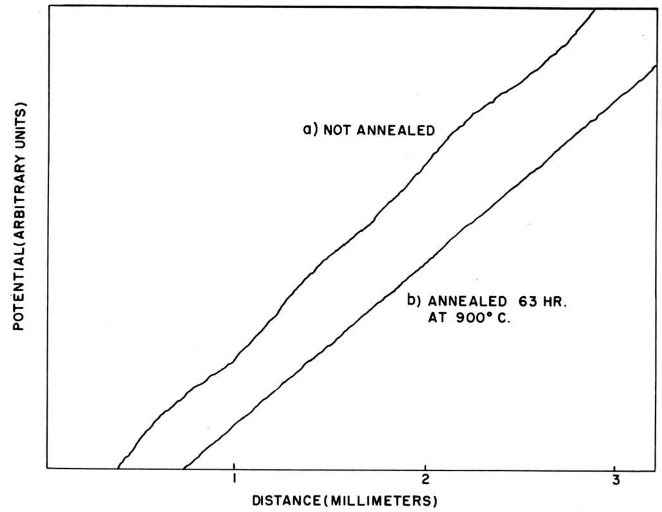

Fig. 1 – Potential scan of two pieces of germanium cut from the same crystal. The slopes of the curves are proportional to resistivity.

operations, but it eliminates the possible introduction of undesired crystal defects during the annealing process.

Fig. 1 shows part of a potential microscan of two samples of germanium which were originally badly striated. The two bars are adjacent strips of the same longitudinal slab. The pieces are about 1.5 cm long and were probed lengthwise. Curve (a) is for one bar

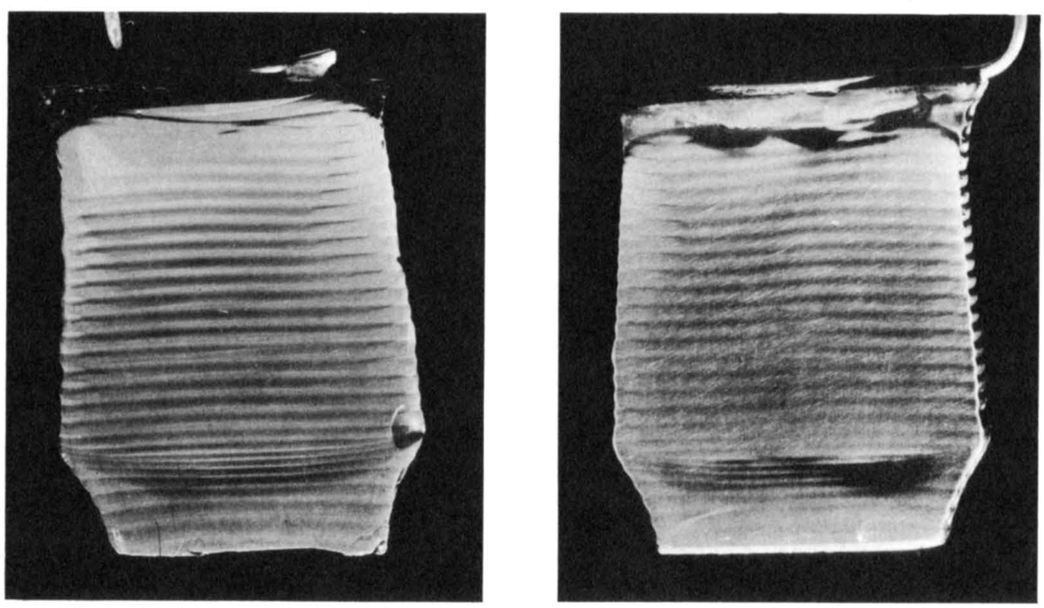

Fig. 2 – Resistivity striations of the two samples of Fig. 1 as revealed by the pulse plating technique. The slab on the left has not been treated. The one on the right was annealed for 63 hours at 900 degrees C.

which was untreated and curve (b) is for the other which had been annealed for 63 hours at 900 degrees C. Curve (a) shows resistivity variations in adjacent zones of the order of 1.8/1. In curve (b) the resistivity variations have been reduced to 1.1/1 or less. Since annealing has been found to reduce hole lifetime, effort should be concentrated on eliminating the cause of striations rather than on suppressing them after they occur.

It is of interest to observe that the copper-plating technique, outlined previously, is sufficiently sensitive to indicate clearly the remanent striations of annealed samples, even though the resistivity variations have been greatly attenuated. Fig. 2 shows the striations in a slab of germanium as they are revealed by the copper-plating technique. The pieces shown are those of Fig. 1. The faces plated are the ones along which the two pieces were originally joined. The slab on the left has not been treated. The one on the right was annealed for 63 hours at 900 degrees C. As is shown in Fig. 1, the resistivity of the annealed slab is much more uniform than that of the unannealed slab. The period of the striations is about 1 mm. Note that the striations in the picture on the left seem to be made up of fine structure while those in the annealed sample seem to show no fine structure.

From diffusion theory, one would expect that an anneal of only 63 hours would not appreciably affect striations with a 1-mm period. However, if the striations are made up of bunches of fine striations, then diffusion is quite adequate to account for the observed changes in measured resistivity. The resistivity scan did not have sufficient resolution to show the fine structure.

P. R. Camp

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