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W. L. Hansen, R. H. Pehl, E. J. Rivet, and F. S. Goulding

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SELECTION OF GERMANIUM FOR LITHIUM-DRIFTED RADIATION DETECTORS BY OBSERVATION OF ETCH-PIT DISTRIBUTIONS

by W. L. Hansen, R. H. Pehl,
E. J. Rivet and F. S. Goulding*

Lawrence Radiation Laboratory
University of California
Berkeley, California

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ABSTRACT

This note establishes the value of observation of etch-pit distributions as a guide in the selection of germanium for use in lithium-drifted germanium detectors. Results are presented showing a very good correlation between the etch-pit distribution and detector performance for a number of crystals pulled on the 111 axis. It is inferred that mechanical strain produced by thermal conditions in the crystal growing process is the major source of potential charge trapping sites in the final detector.

I. INTRODUCTION

Our own observations, and those made by other groups, show that conventional semiconductor material parameters provide no indication of the quality of radiation detectors that can be made from different germanium crystals. Since it was recognised some years ago that very small amounts of oxygen present in crystals result in a serious reduction in lithium drift mobility all germanium now made for detectors is grown in either a reducing atmosphere or vacuum. Furthermore, our general observation that detectors made from vacuum grown crystals exhibit low breakdown voltages and very poor charge collection has led us to growing crystals in a pure hydrogen atmosphere, exclusively. Consequently, the following discussion, for the most part, concerns measurements on crystals pulled in a pure hydrogen atmosphere on the 111 axis, but results are also presented for some zone-levelled crystals grown in forming gas on the 111 axis.

Even with all precautions taken to eliminate oxygen and other known sources of problems, wide variations in performance are observed both between detectors made from different cyrstals, and between detectors made from different parts of the same crystal. In detectors, charge trapping (which may be exaggerated by electric field non-uniformities) has been shown to be the mechanism causing poor performance. The source of these traps has not been clearly established, and may vary from crystal to crystal, but recent work

by Armantrout[1)] indicates that the lithium-defect interaction constitutes one major type of trap. Armantrout has also shown that the infra-red response of detectors can be used as a guide to the "detector" quality of germanium.

As the manufacture of detectors in order to evaluate a crystal is a time consuming, frustrating and expensive process, it is important to find a simple measurement which correlates with detector performance. We have found that etch-pit distributions provide a virtually infallible guide to crystal quality (vacuum grown crystals excepted) for detector use. At least a major source of problems in detectors is revealed by this very simple technique, although we have accurately discriminated between crystals from which detectors showing small differences in performance were made.

II. DISLOCATION ETCHING

Almost any chemical etch which attacks germanium will reveal screw-axis dislocations on the 111 face. However, the overall appearance of the etched faces is greatly variable for most etches. For example, the commonly used CP-4 etch produces sharp, small pits when properly controlled. But if the etch time is too short, lapping damage will be confused with dislocations, and if the etch is too long the pits become rounded. Consequently, we selected a standard etch routine that would be least affected by time-temperature variations. A standard etch routine has the added feature that

variations in etch pit size are due to real variations in the energy distribution around a dislocation rather than to external chemical variables.

The crystal slice is first lapped with 600 grit carborundum and then polish etched* to produce a smooth background with minimum pit size. Since most of the crystals used have a fairly low dislocation density we can develop the etch pits to a large size for unmagnified observation. This is done with a 15 minute Billig [2)] etch† which produces large, sharp pits. Billig etch decomposes on heating in the presence of germanium, and the same solution cannot be used for more than one etching.

The samples are illuminated for photography by placing three lights at an angle of about 60° to the sample surface, and at 120° with respect to one another, and the crystal is rotated to achieve maximum pit brightness.

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* HNO_3:HF: Red fuming HNO_3, 6:2:1

† 12g KOH, 8g K_3 Fe $(CH)_6$ to 100 cc H_2O used boiling

III. TYPICAL RESULTS

The etch-pit photographs for a number of germanium crystals are presented in figs. 1 through 12. These represent a very small selection out of approximately 300 detectors made from nearly 100 crystals (20 commercial and 80 made in our laboratory). The results given here are representative of the larger sample.

The following general observations can be made about the relationship between etch pits and crystal quality:

1. Good material is always characterized by a uniform distribution of etch pits.
2. No clear relation has been seen between the etch pit density and quality except in the case of zero dislocation crystals which are always poor.
3. A ring-shaped area depleted of etch pits always signifies poor material.
4. A minor degree of slip does not seem to be detrimental to detector performance but gross lineage is unacceptable.

The crystals that we have grown have, in general, a similar evolution of the etch-pit pattern. The seed end of the crystal generally has a uniform pit distribution often with minor slip. The slip usually disappears shortly after the full diameter is reached and a uniform, good quality region of variable length follows.

The ring structure depleted of etch pits gradually appears and the quality deteriorates. The tail end almost always shows the ring figure, often with slip.

It is difficult to establish very precise quantitive criteria for the quality of a crystal used for detectors. However, in order to provide the reader with a measure of our criteria, the following rough parameters measured on a 0.8 cm thick, full area device are quoted as representative of a good crystal:

1. Drift current at 35°C: <10 mA/cm^2.
2. Breakdown Voltage: >2 kV on final device.
3. Capacity - Voltage relationship after drift (no clean-up drift): Capacity will increase very little when the voltage is reduced from 1 KV to 100 volts.
4. Performance on ^{60}Co γ-rays: (1.173 MeV peak):

   Full width at half-max:

(quoted for 3 cm dia. slice; slightly worse expected for > 3 cm dia. slice).	<2 keV at 2 KV applied voltage <2.5 keV at 500V applied voltage

Crystals which do not initially meet the drift current and breakdown voltage criteria sometimes do when a skin of material is removed.

With these objectives in mind we will now examine the etch pit photographs in turn:

Fig. 1: A slice of a germanium crystal obtained from Hoboken in 1966 from which outstanding detectors were produced. We have insufficient material to provide an etch-pit distribution profile for the whole length of the crystal; a slice from a known good section is seen here. The etch-pit distribution is reasonably uniform, with no apparent pattern, and a fairly low dislocation density.

Fig. 2: A slice from crystal #40 grown at LRL. The dislocation density is clearly much higher than that of fig. 1, but the distribution is reasonably uniform with only a slight hint of ring structure. Excellent detectors were made from this crystal.

Fig. 3: A slice from crystal #69 grown at LRL. The dislocation density is uniform, and again this crystal made an excellent detector.

Fig. 4: A Hoboken zone-levelled crystal. The uniformity of the etch-pit distribution indicates a high quality crystal, and this is borne out by the high performance detectors produced.

Fig. 5: Another Hoboken zone-levelled crystal. The pronounced ring structure indicates a poor quality crystal, and detectors made from this crystal gave poor performance.

Fig. 6: A Sylvania zone-levelled crystal. The same remarks apply as in fig. 5, with the detectors being completely useless in this case.

Fig. 7: A slice taken near the middle of crystal #70 grown at LRL. The pronounced ring structure indicates a poor quality crystal, and detectors made from the middle of this crystal were not acceptable.

Fig. 8: and Fig. 9: These figures illustrate the changes that can occur along the length of a crystal (LRL #68). Near the head end (fig. 8), some slip is visible but the etch-pit distribution is reasonably uniform, and an excellent detector was made from this slice. Half-way along the length of the crystal (fig. 9) a pronounced ring structure is present and detectors made from this region are worthless. The region between figs. 8 and 9 did produce an excellent coax detector although some ring structure was present. An interesting observation is that we have made good coax detectors from other crystals having a ring structure, although planar detectors made from similar material were quite poor.

Fig. 10, Fig. 11 and Fig. 12: These figures show the behaviour along the whole length of a crystal (LRL #58). The performance of detectors made from this crystal precisely match the predictions based on the etch-pit distributions; the detector made from the head is excellent, detectors from the middle are very poor, while those from the bottom are worthless.

IV. DISCUSSION

While these results are representative of a very useful technique, and they are presented here in that light, it is interesting to speculate on the physical mechanisms involved in the rather direct relationship between the etch-pit distribution and crystal quality for detectors.

We do know that the etch-pits reveal dislocations, and the migration of these dislocations, occurring while the crystal is still in the plastic temperature range, is governed by mechanical strain. One can therefore assume that built-in mechanical strain in the crystal is being observed. The observation of the ring pattern and slip can be related to the work of Billig [2)] and others who discuss the effect of the shape of the liquid-solid interface and plastic deformations during crystal growth. Our results are similar and indicate that further work on thermal profiles in the crystal growing apparatus is necessary.

It has been a general observation that dislocation free crystals are unsuitable for detectors. It is likely that dislocations act as low energy sites to nucleate freezing during crystal growth, and that dislocation free crystals are poor because these low energy sites are produced by vacancy clusters. One can also speculate that in crystals containing dislocations, the vacancies are condensed on a defect of very small cross-section, while in dislocation free

crystals, the vacancies are mobile and may combine with a diffusing lithium ion, a phenomena which can be linked to the work of Armantrout[1].

Since dislocations can only move through the motion of vacancies, it may be that the crystals with the ring structure indicating strain, (i.e., crystals in which the dislocations have moved) have a high density of unbound vacancies or vacancy clusters. This might suggest that crystals with the ring figure would behave like dislocation free crystals on lithium drifting. This line of argument is supported by the work of Brock[3] on anomalous X-ray transmission in germanium.

ACKNOWLEDGEMENT

The work of R. C. Cordi in preparing many of the samples is acknowledged.

FOOTNOTE AND REFERENCES

* This work was carried out as part of the program of the Nuclear Chemistry Division of LRL, Berkeley and was funded by the United States Atomic Energy Commission under contract W-7405-eng-48.

1) G. A. Armantrout, Defect study and identification in Ge(Li) P-N junction radiation detectors, UCRL-71679, September 1969, Proc. Elect. Materials Conf., Boston, Mass. August 1969, (to be published in TMS-AIME).

2) E. Billig, Proc. Roy. Soc., London, A 235, 37 (1956).

3) G. E. Brock, The effect of elastic strain on the anomalous transmission of X-rays in Ge, in Properties of Elemental and Compound Semiconductors, New York, 1960 (Interscience, Wiley) pp. 211 - 224.

FIGURE CAPTIONS

Fig. 1. A Hoboken crystal from which outstanding detectors were produced. The etch-pit distribution is reasonably uniform with no apparent pattern.

Fig. 2. Crystal #40 grown at LRL from which outstanding detectors were produced. The dislocation density is clearly much higher than that of fig. 1, but the distribution is reasonably uniform.

Fig. 3. Crystal #69 grown at LRL from which an outstanding detector was made. Again note the uniform dislocation density.

Fig. 4. A Hoboken zone-levelled crystal. The uniformity of the etch-pit distribution indicates a high quality crystal, and this is borne out by the high performance detectors produced.

Fig. 5. A Hoboken zone-levelled crystal. The pronounced ring structure indicates a poor quality crystal, and detectors made from this crystal gave poor performance.

Fig. 6. A Sylvania zone-levelled crystal. The pronounced ring structure indicates a poor quality crystal, and detectors made from this crystal were worthless.

Fig. 7. A slice taken near the middle of crystal #70 grown at LRL. The pronounced ring structure indicates a poor quality crystal, and detectors made from the middle of this crystal were not acceptable.

Fig. 8. Head end of crystal #68 grown at LRL. Some slip is visible but the etch-pit distribution is reasonably uniform, and an excellent detector was made from this slice.

Fig. 9. Middle of crystal #68. A pronounced ring structure is present and detector made from this region are worthless.

Fig. 10. Head end of crystal #58 grown at LRL. An excellent detector was made from this slice.

Fig. 11. Middle of crystal #58. A very poor detector was made from this slice.

Fig. 12. Tail end of crystal #58. Detectors made from this region are worthless.

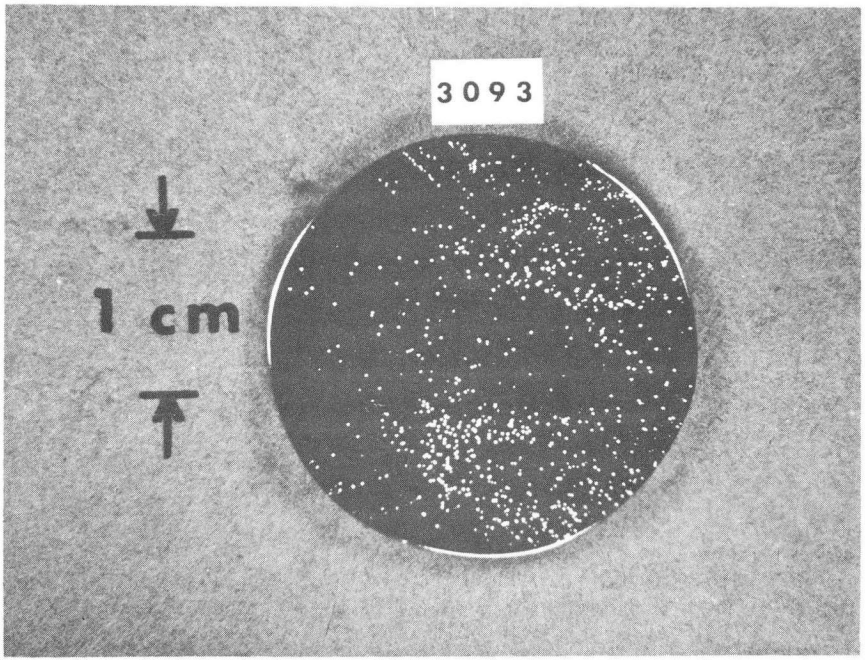

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Fig. 1

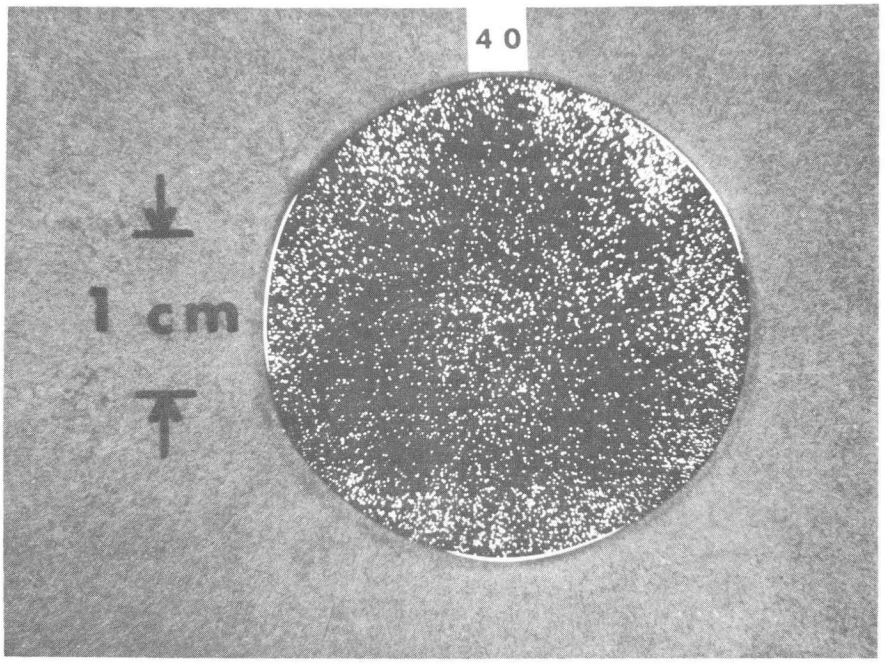

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Fig. 2

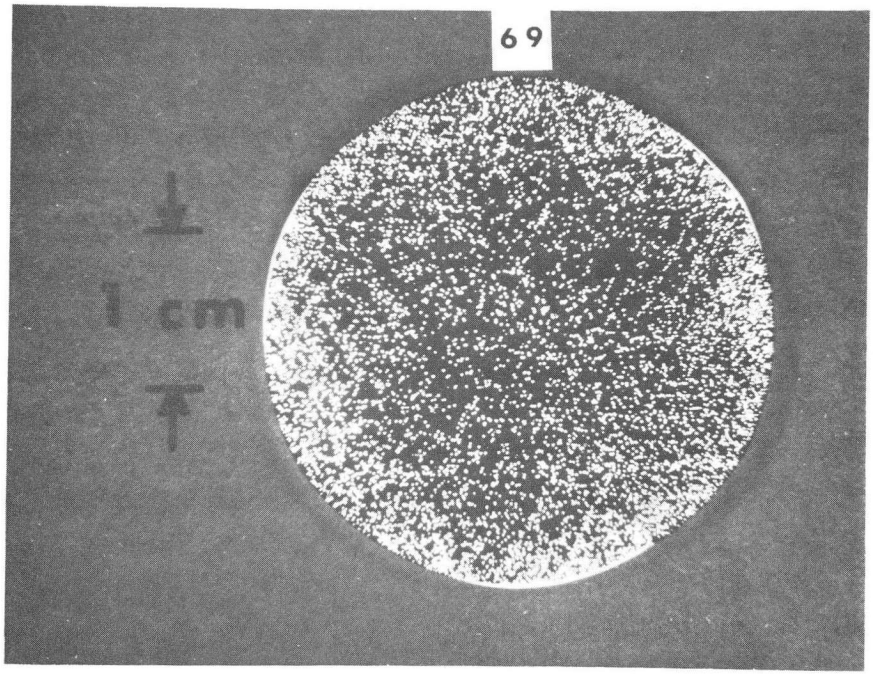

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Fig. 3

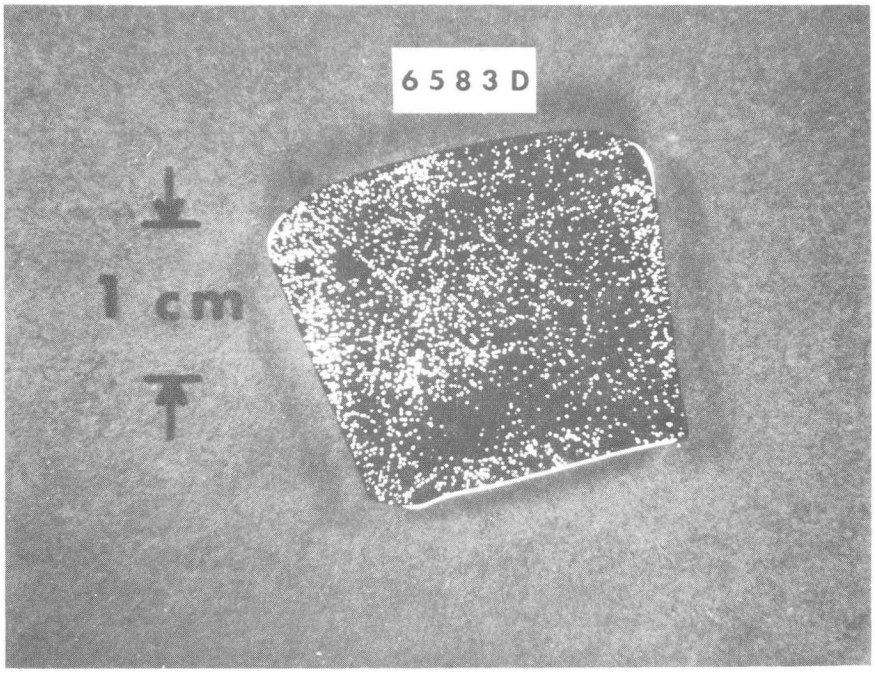

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Fig. 4

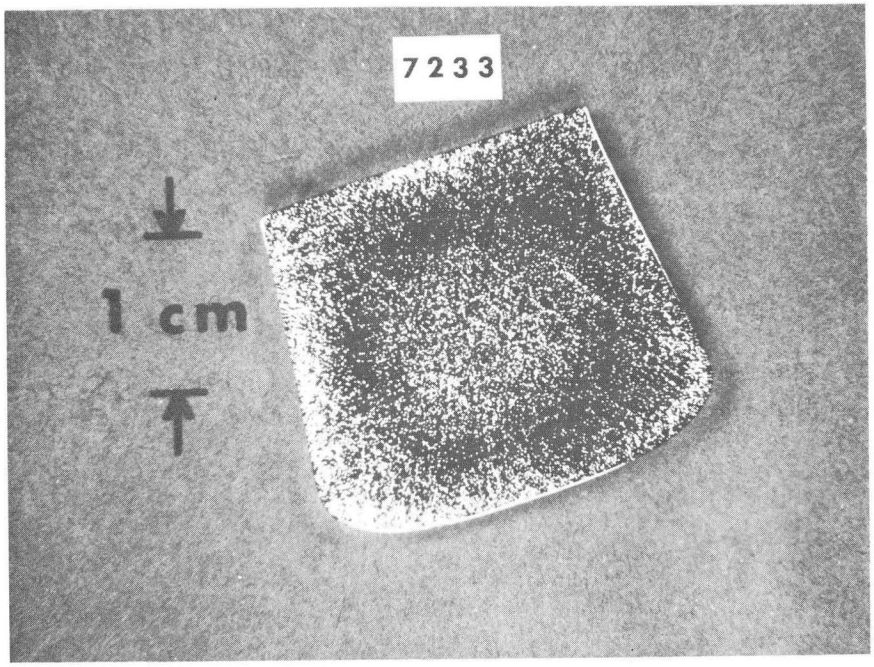

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Fig. 5

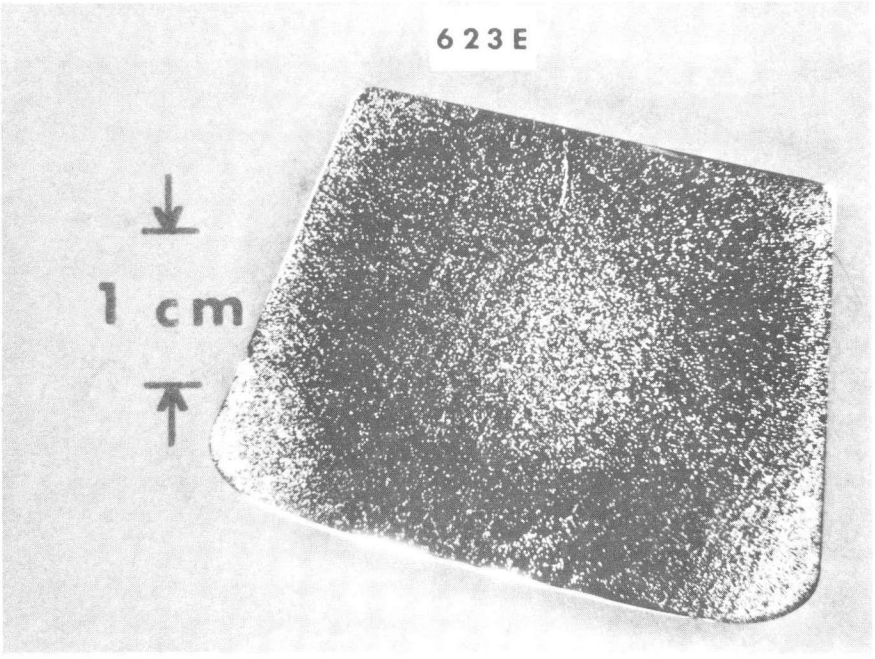

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Fig. 6

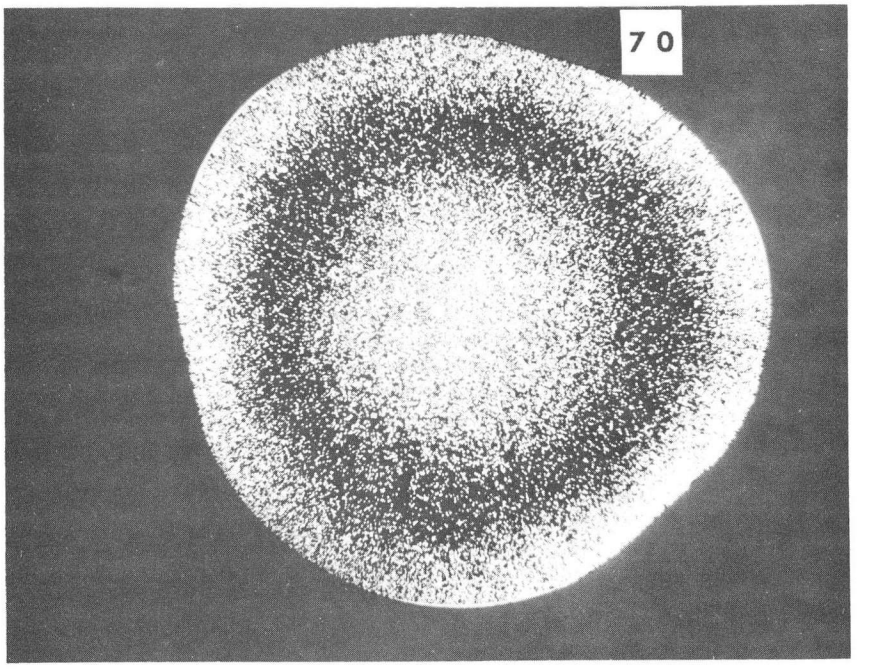

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Fig. 7

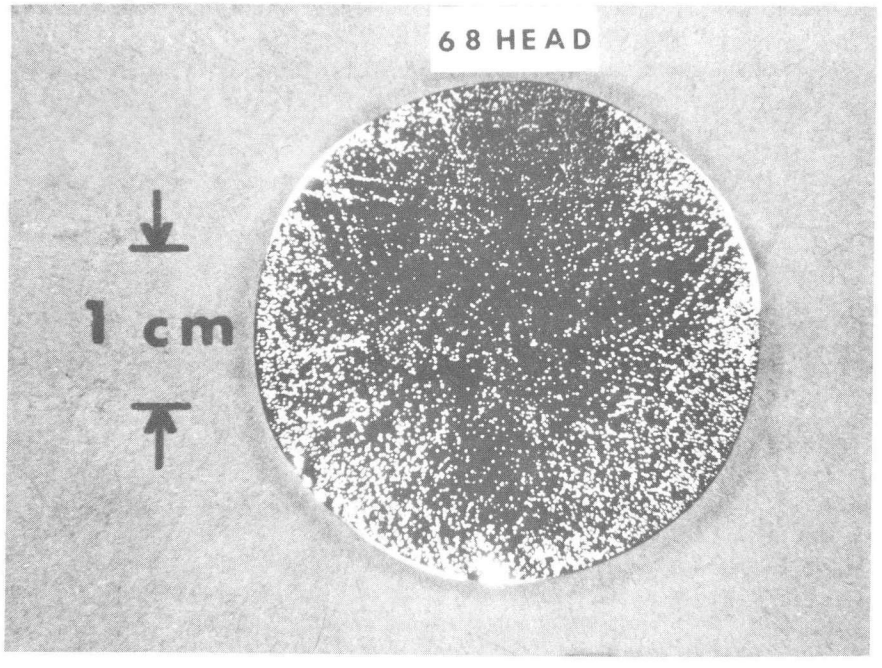

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Fig. 8

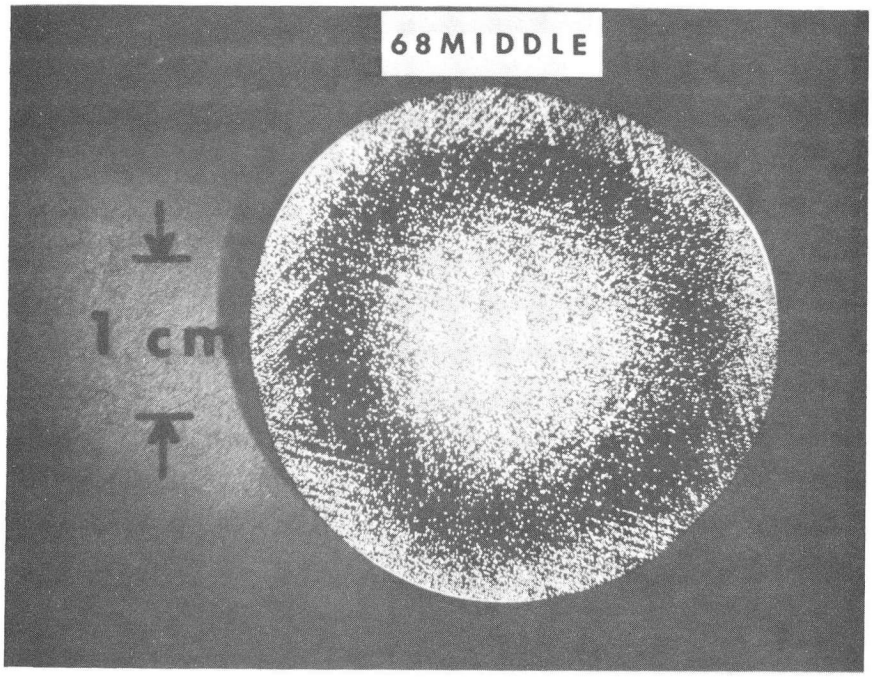

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Fig. 9

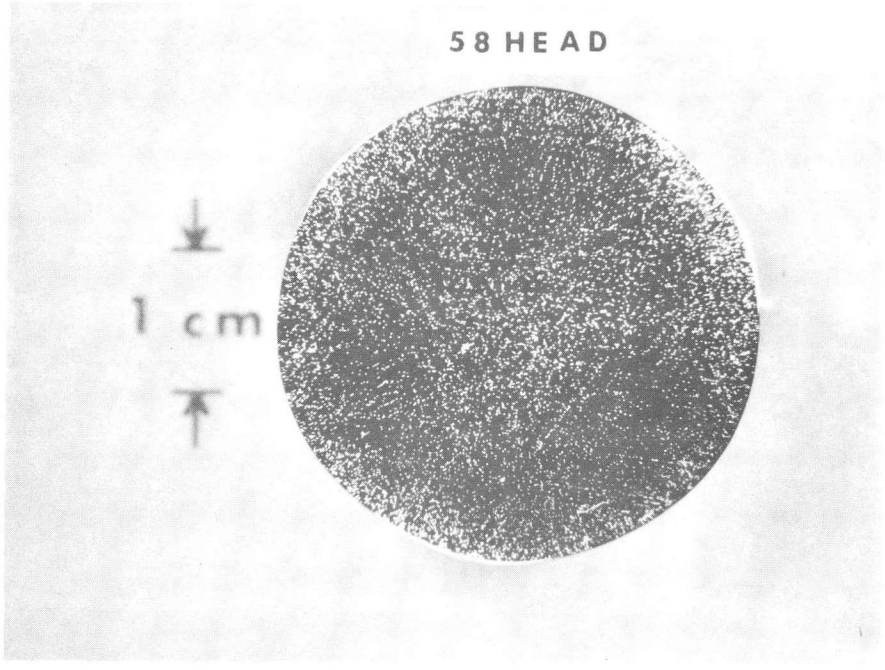

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Fig. 10

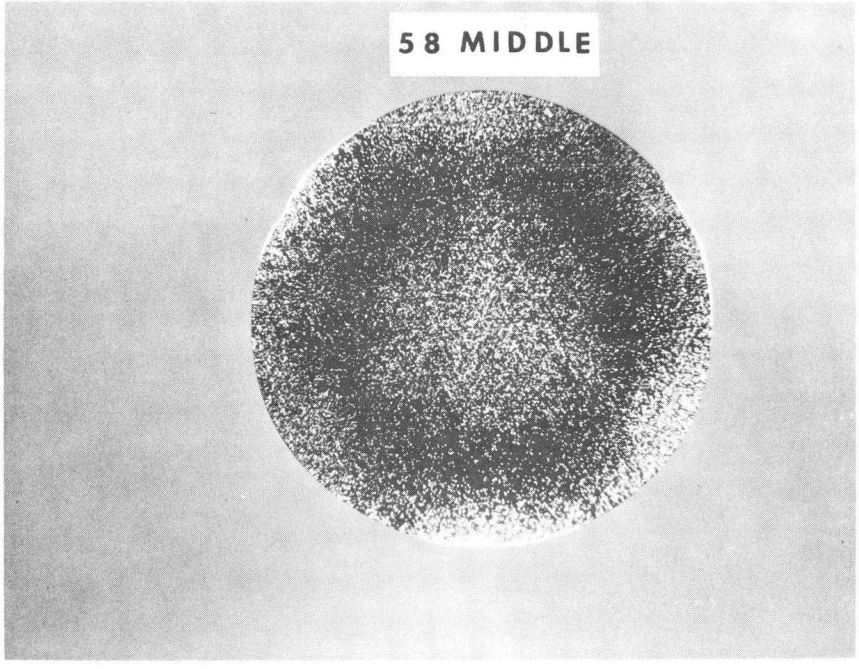

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Fig. 11

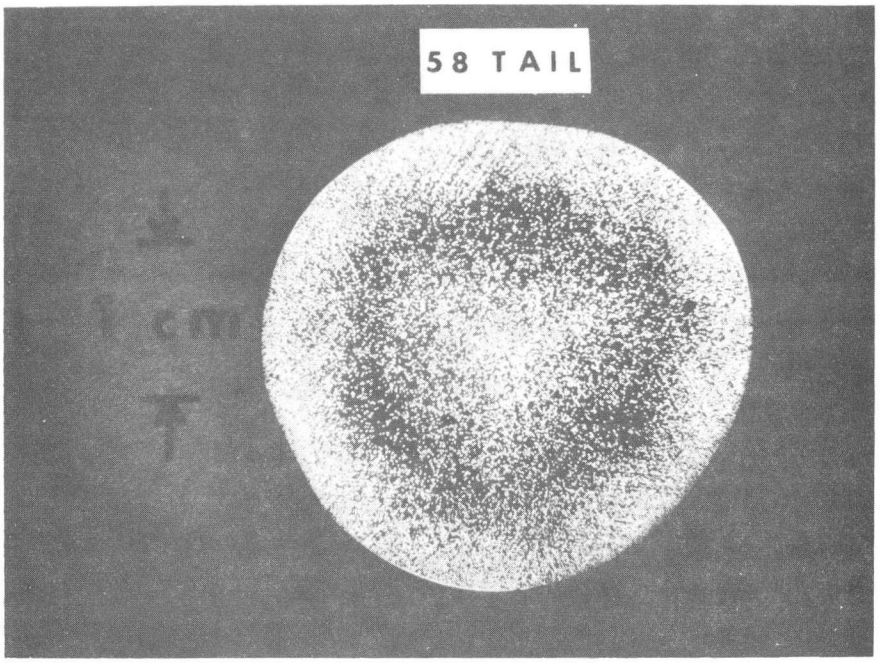

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Fig. 12

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