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HIGH-PURITY GERMANIUM CRYSTAL GROWING

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January 1971

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## HIGH-PURITY GERMANIUM CRYSTAL GROWING

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January 1971

### INTRODUCTION

We have been growing germanium crystals of high-structural perfection for some time for use in making lithium-drifted detectors<sup>1)</sup>. Stimulated by the recent work of R. N. Hall<sup>2)</sup> on high-purity crystals, we thought it would be useful to investigate the possibilities and limitations of our techniques when applied to growing very pure germanium. We originally thought that the lack of facilities to control airborne contamination (by laminar flow work stations, etc.) might make our chances of success very small, but as reported in this paper, initial results indicate that this prejudice was unjustified, and that our previously developed crystal growing techniques were applicable to this work.

## STARTING MATERIAL

The selection of starting material for growing high-purity germanium crystals presents a dilemma. Polycrystalline ingots can be zone refined to high purity by using a large number of zone passes, but measuring the purity of the resulting material is impossible with existing techniques. Refined polycrystalline ingots can be seeded on the final zone pass to give a single crystal whose purity can be measured, but the seeding process almost certainly introduces contamination. Commercially available high-purity germanium includes polycrystalline material that is not measurable, and single crystal that has a higher impurity concentration ( $10^{11}$  to  $10^{12}/\text{cm}^3$ ) than is desirable. While some of our earlier crystals were grown from commercial starting material, we now zone refine our own polycrystalline starting material under conditions thought to be much cleaner than those of the crystal puller, then grow a crystal from this material in a vertical crystal puller.

Starting material for our zone refining consists of ingots of  $10 \text{ cm}^2$  cross-section and 62 cm long. The trapezoidal quartz boat is lined either with carbon smoke made by burning propane, or with silica smoke made by burning a mixture of  $\text{SiH}_4$ ,  $\text{H}_2$  and  $\text{O}_2$ . A 2 cm-wide melted zone is formed by direct coupling to the germanium charge with a single turn 450 KHz R.F. coil that travels along the charge at 11 cm/hr. About 20 zone passes are made. Since the RF fails to couple to intrinsic germanium at room temperature, each zone pass is started by heating the head

end of the ingot with a hand touth. We find that only about the last cubic centimeter of charge to freeze shows extrinsic conductivity at 25°C.

#### CLEANING PROCEDURE

A standard procedure has been used throughout for cleaning all quartz and germanium. The piece is hand held with a polyethylene outer glove over an inner rubber glove, and is rotated under a stream of 5:1  $\text{HNO}_3$ :HF, then deionized water, then 6:1:1  $\text{H}_2\text{O}$ :HCl: $\text{H}_2\text{O}_2$ ,<sup>3)</sup> and finally, a stream of deionized water. The work and glove is immediately blown dry with nitrogen, and the work is placed in the crystal grower using the same glove. The crucible is preheated to about 1100°C in the crystal growing ambient gas, then is allowed to cool to room temperature, shortly before the germanium charge is inserted.

#### CRYSTAL GROWING

With the exception of the heat shielding, the crystal grower is identical with that previously reported<sup>1)</sup> and is shown in Fig. 1. The ambient gas is either hydrogen, nitrogen or mixtures of these at 3 liters/min. and the flow path is as indicated by the arrows in Fig. 1. The 1,0,0 oriented seed is rotated at 40 RPM, the susceptor at 2 RPM

and the pull rate is about 12 cm/hr. Typical charges used up to the present time are about 800 g., and the pulled crystals have diameters between 24 and 36 mm. Most crystals have been held to almost constant diameter by varying the temperature of the melt, and have almost circular cross-section for the entire length. The melt was grown to depletion during the pulling operation to avoid breakage of the quartz crucible.

#### RESULTS

The net ionized charge concentration in the pulled crystals is determined by measuring the resistivity and also by determining the punch-through voltage of diodes made from the crystal. The resistivity is found by passing 10 to 1000  $\mu$ a of current through the crystal and recording the voltage measured by probes at intervals of 1 or 2 cm along a sand blasted strip after applying a thin Ga-In eutectic to the ends and immersing in liquid nitrogen. Test diodes are made by diffusing lithium at about 375°C into one side of a 4 to 6 mm thick slice of the crystal and evaporating gold on the other side (previously etched). The punch-through voltage is measured by observing the amplitude spectrum of pulses due to  $^{207}\text{Bi}$  conversion electrons hitting the detector through the gold face.

Typical impurity profiles as derived from resistivity measurements are shown in Figs. 2, 3 and 4. To date, all crystals have been p-type at the seed-end and n-type at the tail. The crystal grower ambient

gases tested did not appear to affect either the magnitude or type of impurity. Etch-pit density<sup>4)</sup>, in the few cases we have measured, is 10 to 100/cm<sup>2</sup> for at least 90% of the crystal length and is uniformly distributed.

Examples of diode capacity-voltage characteristics are shown in Figs. 5, 6 and 7. In Fig. 5, 800 V knee in the capacity-voltage curve corresponds to the punch-through voltage of the diode as measured by <sup>207</sup>Bi electrons through the gold-surface barrier, and the derived impurity concentration ( $5 \times 10^{10}$ ) agrees with that from the resistivity measurement. On the other hand, the apparent punch-through voltage of the diode in Fig. 6 is at 135 V when observed with <sup>207</sup>Bi electrons, but at 250 V from the C-V curve. The impurity concentration ( $2 \times 10^{10}$ ) derived from the resistivity measurement agrees with the 135 V punch-through value. A similar case is shown in Fig. 7, in which the <sup>207</sup>Bi measurement gives a much lower value for the punch-through voltage than is indicated by the knee in the capacity curve. The impurity concentration is  $2 \times 10^9$  according to the punch-through measurement, but the resistivity measurement indicates a value of  $2 \times 10^{10}$ .

One of the incentives for developing high-purity germanium has been the expectation that this material would be free from the charge-trapping often seen with lithium-drifted germanium--particularly with high-energy radiation. This expectation seems to be justified by most of our present observations although serious charge trapping has been observed in one crystal.

A  $^{207}\text{Bi}$  spectrum is shown in Fig. 8. The source is uncollimated and illuminates the entire 10 x 10 mm area of the detector. The peaks have a symmetry equal to the best seen with lithium compensated detectors--this result is typical of high-purity detectors observed to date.

Further confirmation of freedom from charge-trapping has been observed in one detector with high-energy protons. Reasonably symmetrical peaks of 19 keV FWHM were observed with a 6 mm thick detector viewing a 40 MeV proton beam. Another illustration of the value of high-purity germanium has been obtained in measurements on a detector at low temperature (1°K). The work of Martini, et al<sup>5)</sup>, shows that severe trapping from impurities occurs below 15°K in lithium-drifted germanium detectors. However, symmetrical peaks of 40 keV FWHM have now been observed at 1°K from  $^{241}\text{Am}$  alpha particles with a high-purity germanium diode in a system capable of only 40 KeV electronic resolution<sup>6)</sup>.

#### CONCLUSIONS

We have shown that high-purity germanium crystals can be grown with rather simple precautions against airborne contamination. Since there is so little variation in impurity type and distribution from crystal to crystal, a constant source of contamination is suspected--possibly the quartz crucible in which the germanium is melted.

Of the methods used by us to measure the net impurity concentration, the collection of charge from electrons passing through the back surface of a detector is the only accurate one. The impurity concentration derived from capacity measurements is subject to uncertainties due to the surface treatment of the diode. The impurity concentrations derived from resistivity measurements agree reasonably well with those obtained with electron measurements on detectors, but large differences are seen when impurity concentrations are less than  $3 \times 10^{10}$ /cc. One possibility is that this is the result of the heating to form the lithium contact. We have observed a factor of two increase in the impurity concentration after heating a sample to 425°C in argon for three minutes.

As expected, present indications are that trapping problems in high-purity crystals are much less serious than in lithium-drifted germanium.

#### ACKNOWLEDGEMENT

We gladly acknowledge the help of R. Davis in construction and maintenance of the crystal grower. R. Cordi and R. Pehl were responsible for the detector fabrication and measurements mentioned in this paper, and will report separately on some of their results. This work has benefited at every stage by the interest and guidance of F. S. Goulding. This work was performed as part of the program of the Nuclear Chemistry Division of the Lawrence Radiation Laboratory, Berkeley and was supported by the U.S. Atomic Energy Commission, Contract No. W-7405-eng-48.

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- 2) R. N. Hall, To be published in IEEE Trans., NS-18, No. 1 (1971).
- 3) W. Kern and D. Puotinen, RCA Review, Vol. 31, No. 2 (1970) p. 187.
- 4) A fast etch for pits on 1,0,0 germanium was suggested by R. N. Hall. 1:HNO<sub>3</sub>, 2:HF and 1:10% Cu(NO<sub>3</sub>)<sub>2</sub>, this etch was originally due to J. P. McKelvey and R. L. Longini, J. Appl. Phy. Vol. 25,(1954) p.634
- 5) M. Martini, T. McMath and I. Fowler, IEEE Trans. Nuc. Sci, NS-17, No. 3 (1970) p. 139.
- 6) This observation was made by Art Soinski, Lawrence Radiation Laboratory Berkeley, using one of our detectors.

FIGURE CAPTIONS

Fig. 1 Crystal Puller

Fig. 2 Impurity Distribution, crystal #126

Fig. 3 Impurity Distribution, crystal #127

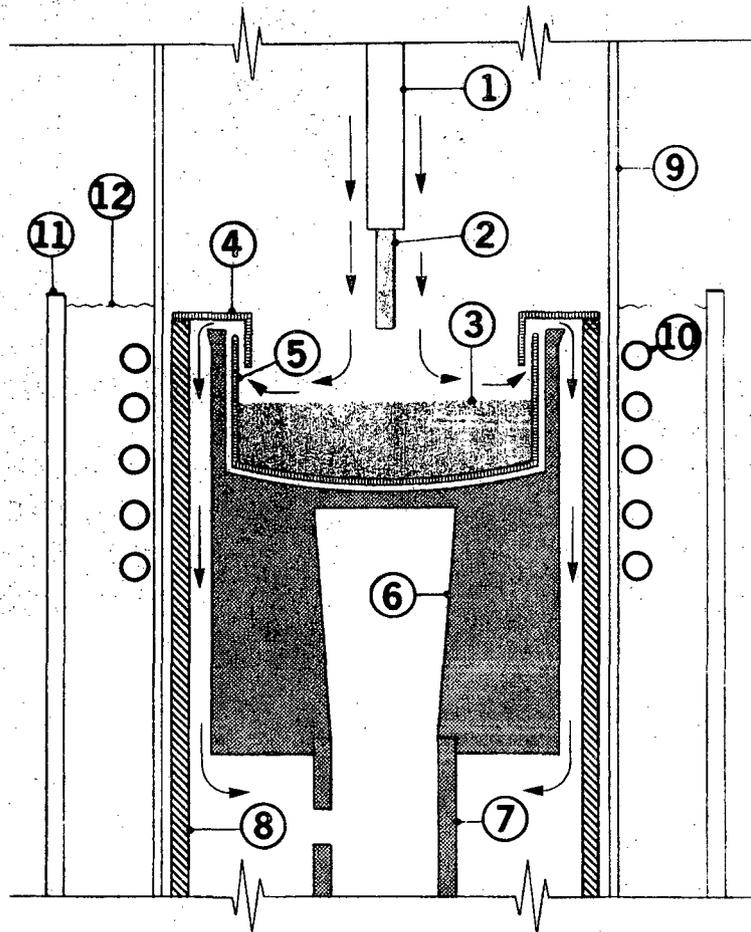
Fig. 4 Impurity Distribution, crystal #133

Fig. 5 Diode capacity-voltage characteristic, diode #127-13

Fig. 6 Diode capacity-voltage characteristic, diode #127-18

Fig. 7 Diode capacity-voltage characteristic, diode #127-20

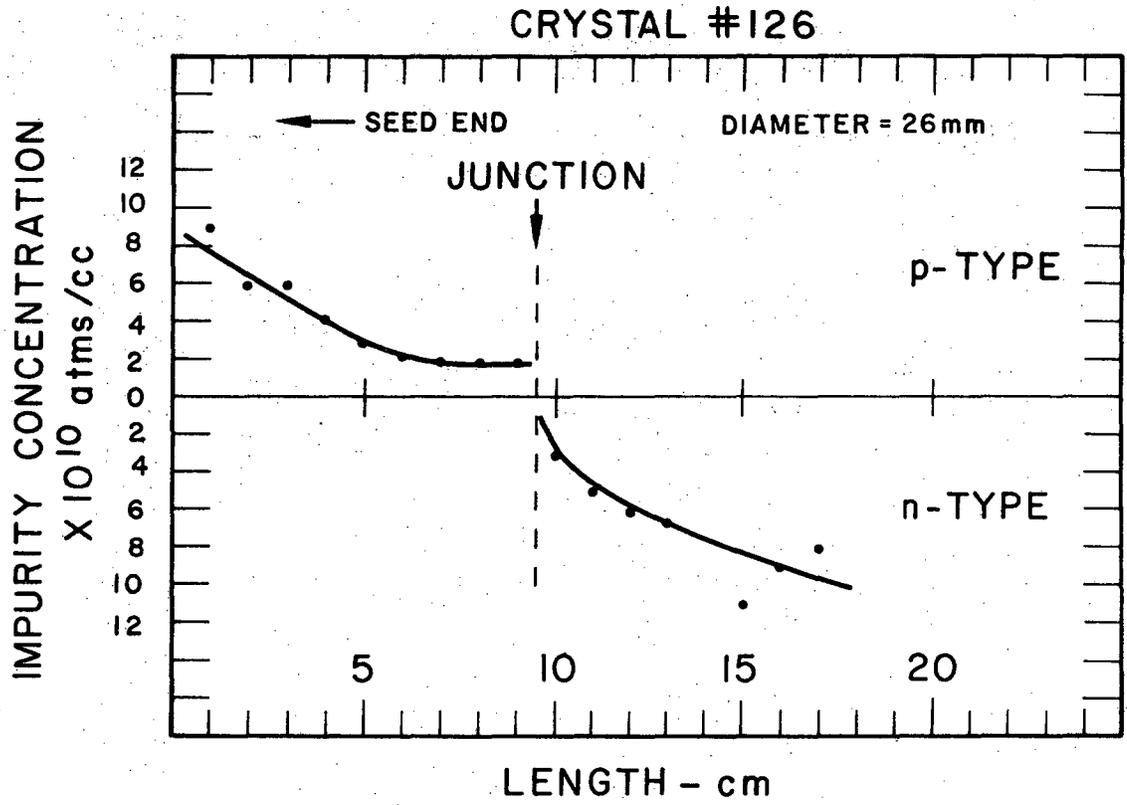
Fig. 8 Spectrum of  $^{207}\text{Bi}$ .



- |                         |                              |
|-------------------------|------------------------------|
| 1. MOLYBDENUM SEED ROD  | 7. CARBON SUSCEPTOR PEDESTAL |
| 2. SEED                 | 8. SAND QUARTZ HEAT SHIELD   |
| 3. GERMANIUM MELT       | 9. QUARTZ OUTER ENVELOPE     |
| 4. QUARTZ GAS DEFLECTOR | 10. R.F.COIL                 |
| 5. QUARTZ CRUCIBLE      | 11. PYREX FISHBOWL           |
| 6. CARBON SUSCEPTOR     | 12. DEIONIZED WATER          |

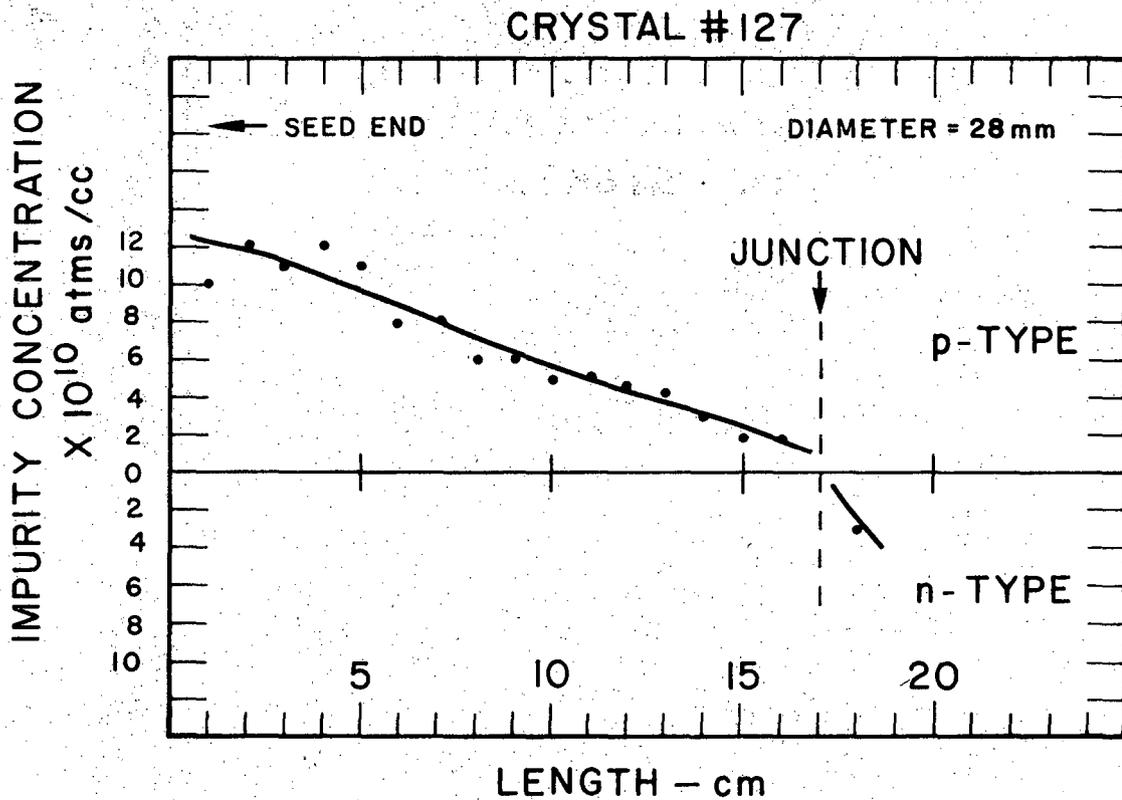
XBL 711-73

FIG. 1



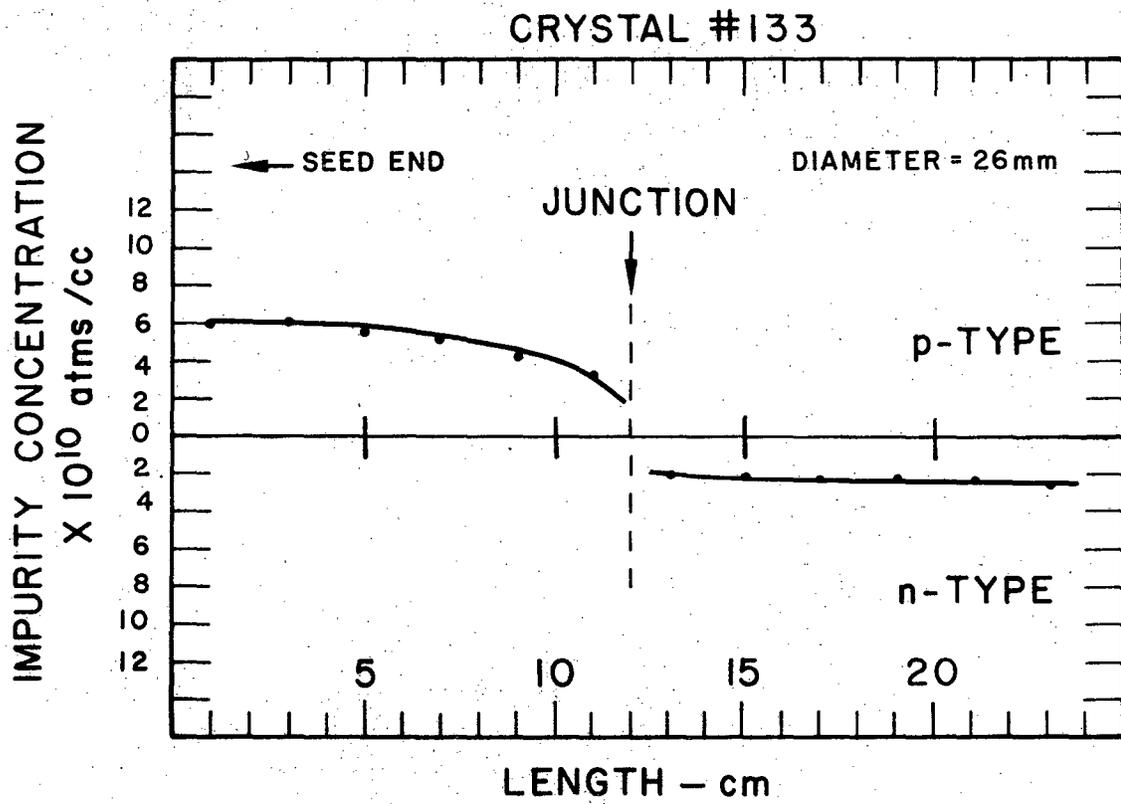
XBL 711-105

FIG. 2



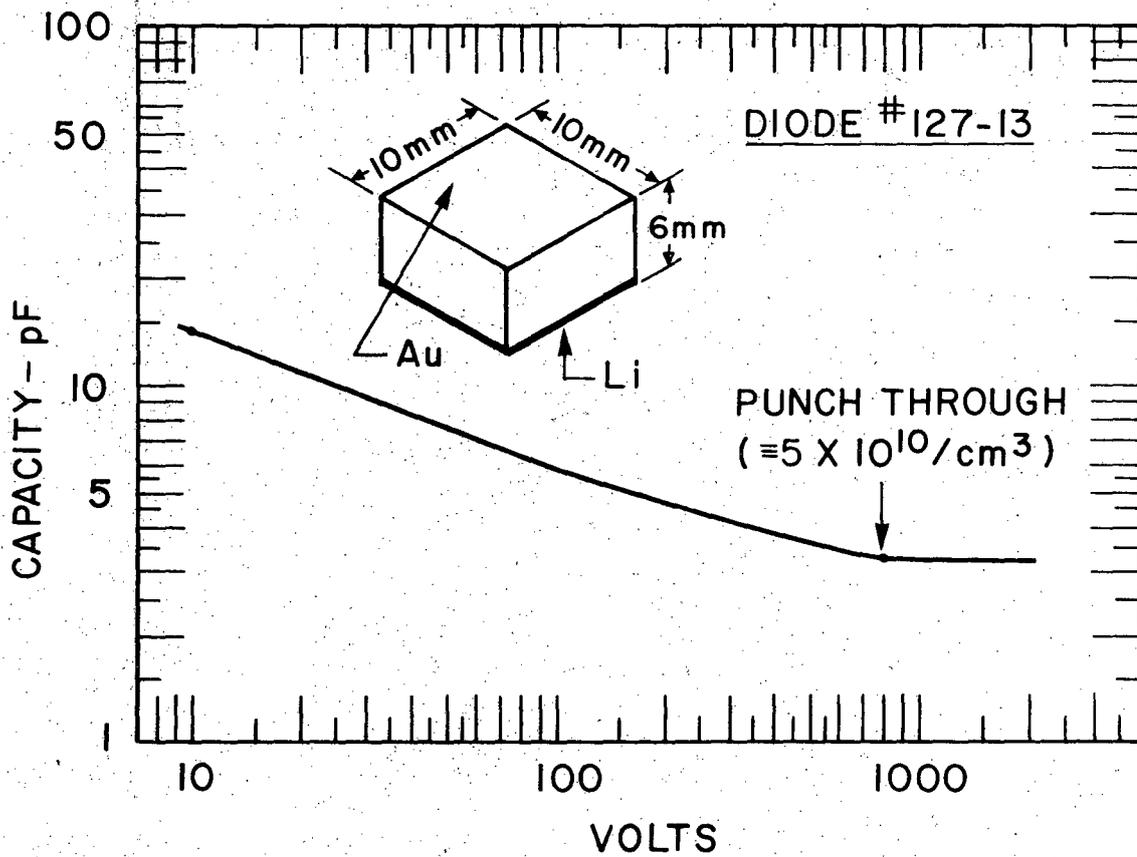
XBL 744-109

FIG. 3



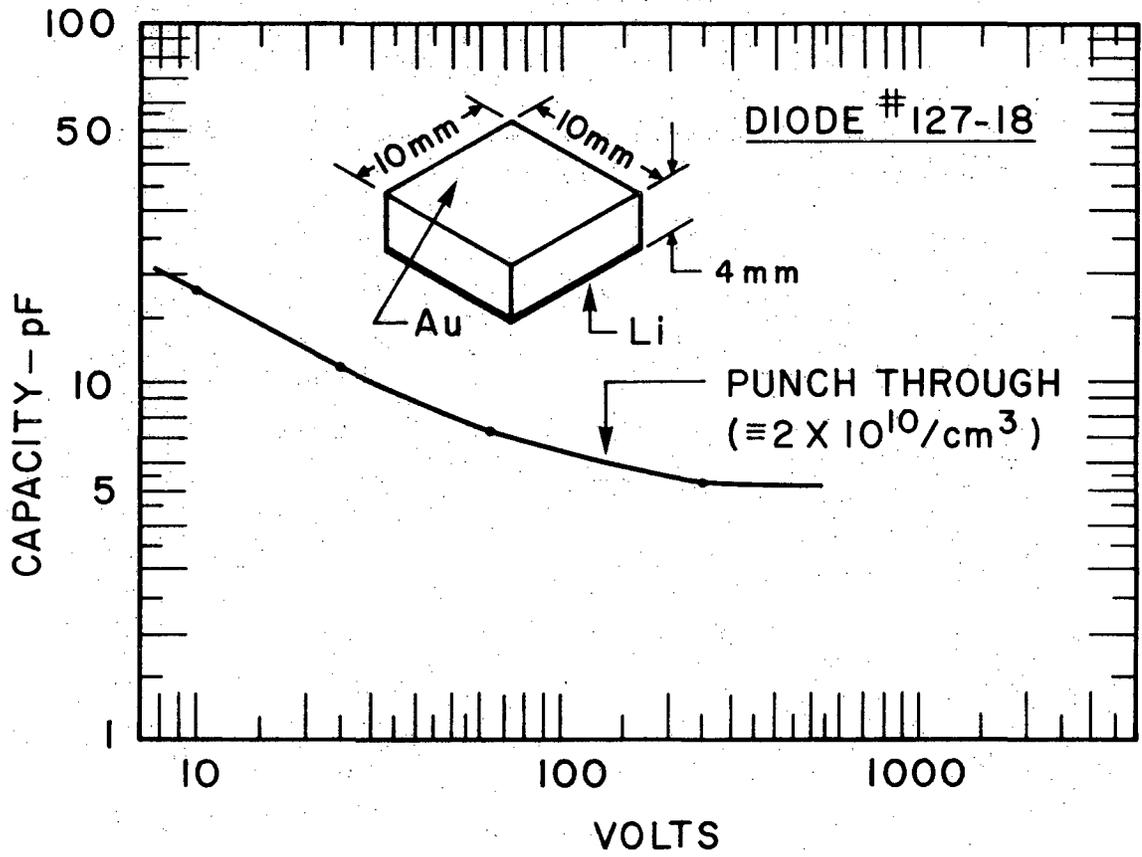
XBL 711-110

FIG. 4



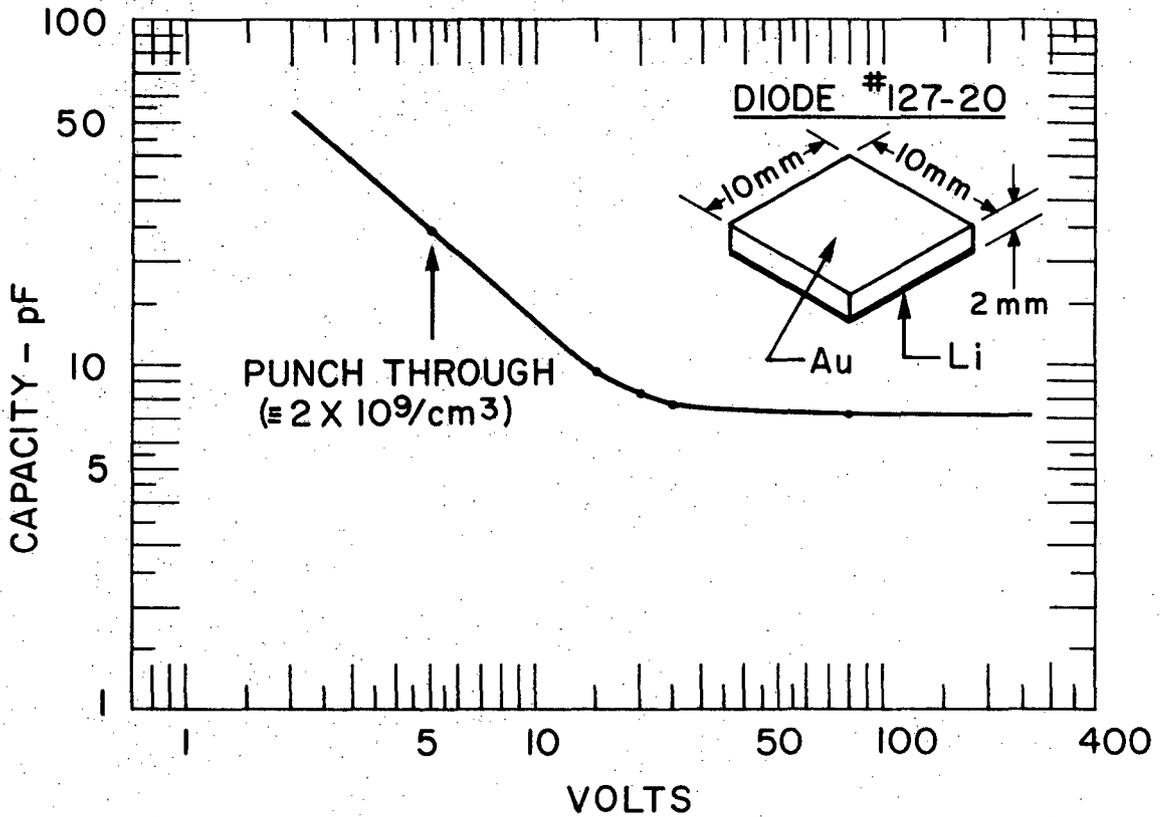
XBL 711-107

FIG. 5



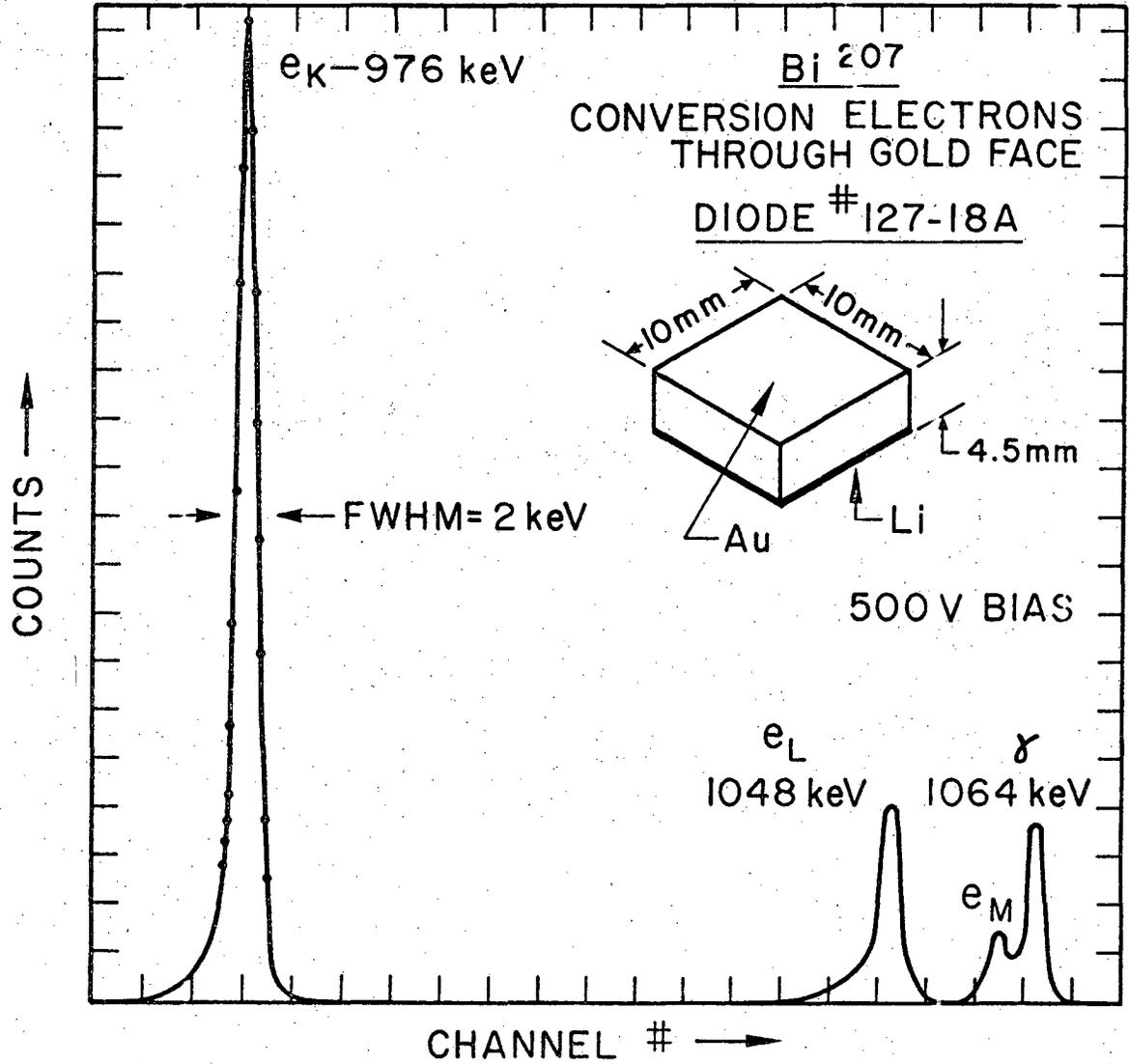
XBL 711-106

FIG. 6



XBL 711-108

FIG. 7



XBL 711-104

FIG. 8

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