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A TECHNIQUE FOR DRIFTING LITHIUM INTO GERMANIUM

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A. Introduction

Methods of drifting lithium into single crystals of germanium have been studied in order to explore the techniques of preparing gamma ray detectors. When lithium is drifted into p-type germanium a diode is produced with a large intrinsic region between its p and n layers. A reverse bias is applied across the device and when gamma rays enter the intrinsic region, they lose energy and produce electron-hole pairs which are collected at both ends of the diode. A pulse of charge is thus created which is proportional in magnitude to the energy of the incident gamma ray. By determining the height of this pulse, an accurate measurement of the gamma ray energy can be obtained.

Several groups are now carrying out studies of drifting lithium into germanium for the purpose of making gamma ray detectors, and there are published reports on their progress.[1,2] We have carried out drifting in a bath of normal pentane in the same manner used by Saunders and others.[3]

In this paper a simple system is described which has been used successfully to drift lithium into germanium, and results of the work with different samples of germanium are presented.

B. Description of Drifting Operation

The two principle suppliers of high purity germanium single crystals are Sylvania[4] and Hoboken.[5] They supply material doped with either gallium or indium, and the ingots of the p-type germanium have a maximum cross section of about 6 cm^2 and are oriented along the [111] plane. The properties of the material varied greatly from ingot to ingot, probably because of uncontrolled variations of certain impurity concentrations. Oxygen impurity is especially to be avoided because oxygen is known to inhibit the drifting of lithium into the sample.[6] Impurities of gold and copper should also be avoided since these impurities cause large leakage currents which result in poor resolution when the sample is used as a gamma detector.[7]

The germanium is cut into the desired size by using either a diamond saw or a wire saw. Before cutting, the sample is glued on either a ceramic or graphite block with a wax,[8] and care must be taken in handling the germanium to avoid cracking the sample. The cut should be as smooth as possible to minimize the subsequent polishing (or lapping) time.

The lithium is then applied to the surface of the germanium, and diffused a short distance (1 mm) into the p type germanium. We used lithium in an oil suspension which was applied easily to the sample, and the sides of the sample were coated with aquadag to make certain that lithium would not come in contact with the sides of the sample during diffusion. Diffusion was done at 450°C in a furnace which is shown in Fig. 1.[9] Nitrogen gas was slowly passed through the system during diffusion to remove oxygen which could react with the lithium on the sample.

Since germanium is brittle, care must be taken to avoid large thermal gradients in the sample which might build up internal stresses that can crack the sample. Therefore the sample is heated in a two step process, first by inserting it only a few inches inside the glass tube where the temperature gradient is such that this position has a temperature of about 200°C. At this temperature the rate of diffusion is slow, but the sample is slowly heated and the oil from the lithium suspension is driven off. After 30 minutes, the sample is placed in the center of the oven for

5 minutes and the lithium then diffuses approximately 1 mm into the germanium.

Following diffusion, the sample is quenched by moving it back to the edge of the glass tube, and the flow rate of nitrogen is increased to cool the sample. After ten minutes, the sample is removed from the oven and further cooled by a jet of air.

The material was lapped on 320 grit grinding paper, followed by a second lap on 400 grip paper and a third lap on 600 grit paper.[10] The purpose of lapping is to remove all deep scratches on the sample which were introduced during the cutting and earlier handling.

The lapping operation gives a rough finish to the surface of the sample, and a smooth mirror-like finish is obtained by a chemical polish. After lapping, the sample is ultrasonically cleaned for one minute, washed in trichloroethylene, and then rinsed in methyl alcohol. At this point and hereafter, the sample is always handled by teflon tweezers. The sample is then chemically polished (etched) in CP4 solution which is composed of (all chemical were reagent grade)

15 parts of 50% HF solution
20 parts of concentrated HNO_3
15 parts acetic acid
3/10 part bromine

The length of time used for etching depends on how fine a polish is required, but is never greater than two minutes. The etching is done by first pouring enough CP4 solution into a plastic beaker to cover the sample. The sample is then dropped into the beaker, and the beaker is slowly agitated by hand to avoid pitting on the sample's surface. When the etch is completed, the process is quenched by adding methyl alcohol to the etchant, and the sample is quickly removed from the beaker and placed in methyl alcohol. At this point the sample has a very fine finish, and the finish is preserved by keeping the sample under methyl alcohol.

The sample is now ready for drifting, and the drifting apparatus which was used is shown in Fig. 2. The pentane bath is used to maintain a constant temperature at the pentane boiling point of 36°C. Other solutions have been considered as a bath, but pentane seems to be best because of its low boiling point and zero dipole moment which minimizes its interaction with the sample. The sample is first removed from the methyl alcohol and sandwiched between two copper plates. The whole assembly is held together by nylon screws, and between the copper and sample is a thin layer of indium which was ultrasonically soldered to the copper. After the assembly is blown dry in nitrogen and immersed in the pentane bath, a potential is slowly applied across the sample by means of a rheostat on the power supply and the polarity of the potential is such that the sample is reverse biased. Our samples were generally 1 cm thick by 2 cm^2 and would hold a 500 volt potential while drawing 15 milliamps of current, but the maximum potential which the sample would hold varied greatly with different initial materials. We sometimes found that the sample would hold only a few hundred volts at the beginning of drift, but after 24 hours a 500 volt potential could be applied without breakdown (no longer hold voltage). The current in the heating mantle surrounding the pentane flask was controlled by a rheostat, and it was adjusted such that the pentane was held at a slow boil. With this arrangement we found that the sample could be drifted for periods up to ten days without breakdown. Occasionally the sample would breakdown, but this was remedied by cleaning the sample with the CP4 etchant. A second etch was also useful if the sample would not hold voltage at the beginning of drift.

Two tests were found useful while working with the sample. One was a hot point probe which indicates whether the sample is n type or p type, and we found that a satisfactory reading was obtained by placing the probe across a microammeter. We also used copper plating to determine the drift depth of lithium into germanium. The sample is reverse biased and placed in a 25 gm/liter solution of $CuSO_4$ such that 25 milliamps flows through the sample. When removed from the plating solution, a thin copper line can be observed along the junction between the drifted lithium and the n type germanium.

C. Results

We attempted to drift lithium into three different samples of germanium. These samples are numbered I, II, and III, and their properties are listed in Table I. We were unable to drift lithium into sample I, so we analyzed the sample by both neutron activation and infrared absorption for the presence of oxygen. Fox has demonstrated that oxygen impurities in germanium will inhibit the drifting of lithium, and he suggested a LiO^+ complex was formed which makes the lithium immobile.[6] The results of the neutron activation analysis are given in Table II, and the presence of a high concentration of oxygen was confirmed in the infrared absorption analysis. We were able to drift lithium into sample II, but the rate of drift was very slow and after two weeks the drift was only 3 mm. Sample III was easily drifted, and depths of 5 mm were attained after 10 days.

To speed the drift rate, we tried to drift at a higher temperature by using a benzene (boiling point of 80°C) bath. But at this temperature, the sample became intrinsic and would not hold a reverse bias. It is possible that this technique would be useful if the bath could be maintained at a lower temperature.

D. Conclusions

We have found a large variation in the performance of samples taken from different ingots. For a given ingot we were able to obtain the same results with different samples, so we attribute the fluctuations in performance to the original ingot and not to variations in our techniques of fabrication. Different ingots have different compositions of impurities, and the lithium drift mechanism must be very sensitive to the presence of these impurities. Consequently when purchasing an ingot of germanium from the manufacturers, one can rarely be certain that it will make a good detector until a sample of the ingot has been successfully drifted. Therefore it is suggested that in future tests, crystal growth and doping be carried out in the laboratory in order to assure uniform quality in material.

E. Acknowledgments

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2. H. M. Mann, F. J. Janarek and H. W. Helenberg, IEEE Transactions on Nuclear Science, July 1966, page 336.
3. E. Saunders, private communication; and F. Cappellani, W. Fumagalli and G. Restelli, Nuclear Instruments and Methods, 37, 352 (1965).
4. Sylvania material can be purchased from Sylvania Electric Products, 1811 Adraian Road, Burlingame, California.
5. Hoboken material can be purchased from Nucleonic Products Co., Inc., 3133 East 12th Street, Los Angeles, California, 90023.
6. R. J. Fox, IEEE Transactions on Nuclear Science, June 1966, page 367.
7. E. Saunders, private communication.
8. The wax we used was the hard grade of Sticky-Wax produced by Corning Rubber Co., 578 Gate Street, Brooklyn, New York. This wax has a melting point of 75°C.
9. The furnace was made from an internally wound Alundum core purchased from the Norton Company, Worcester 6, Massachusetts.
10. The grinding paper was obtained from Buehler Ltd., 2120 Greenwood Street, Evanston, Illinois.

Table I. Comparison of sample properties
(All samples were gallium doped (p type))

Sample	I	II	III
Supplier	Sylvania	Hoboken	Sylvania
Lot number	667 H-7	6782	678F-7
Resistivity (Ω-cm)			
Maximum	18.5	30	13.5
Minimum	10.5	24	8.8
Lifetime (μsec)	100	520	80
Dislocation density (pits/cm^2)			
Maximum	1200	700	1600
Minimum	600	500	1100

Table II. Quantitative analysis of sample I

Impurity	Amount Present
Oxygen	73±22 parts per million (neutron activation)
Iron	14±3 μgm/gm (chemical analysis)
Nickel	0.12±0.03 μgm/gm
Copper	$<$ 0.011 μgm/gm
Silver	$< 6.1 \times 10^{-2}$ μgm/gm
Gold	$(6.8 \pm 0.5) \times 10^{-3}$ μgm/gm

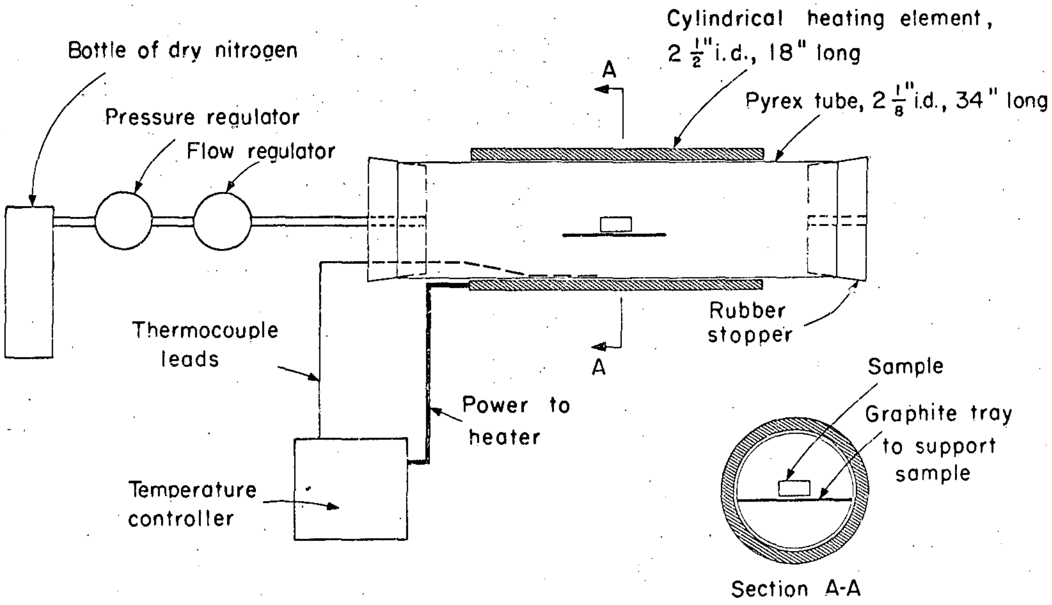

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Fig. 1. Oven used to diffuse lithium into germanium. The sample was placed in the pyrex tube by removing the rubber stopper.

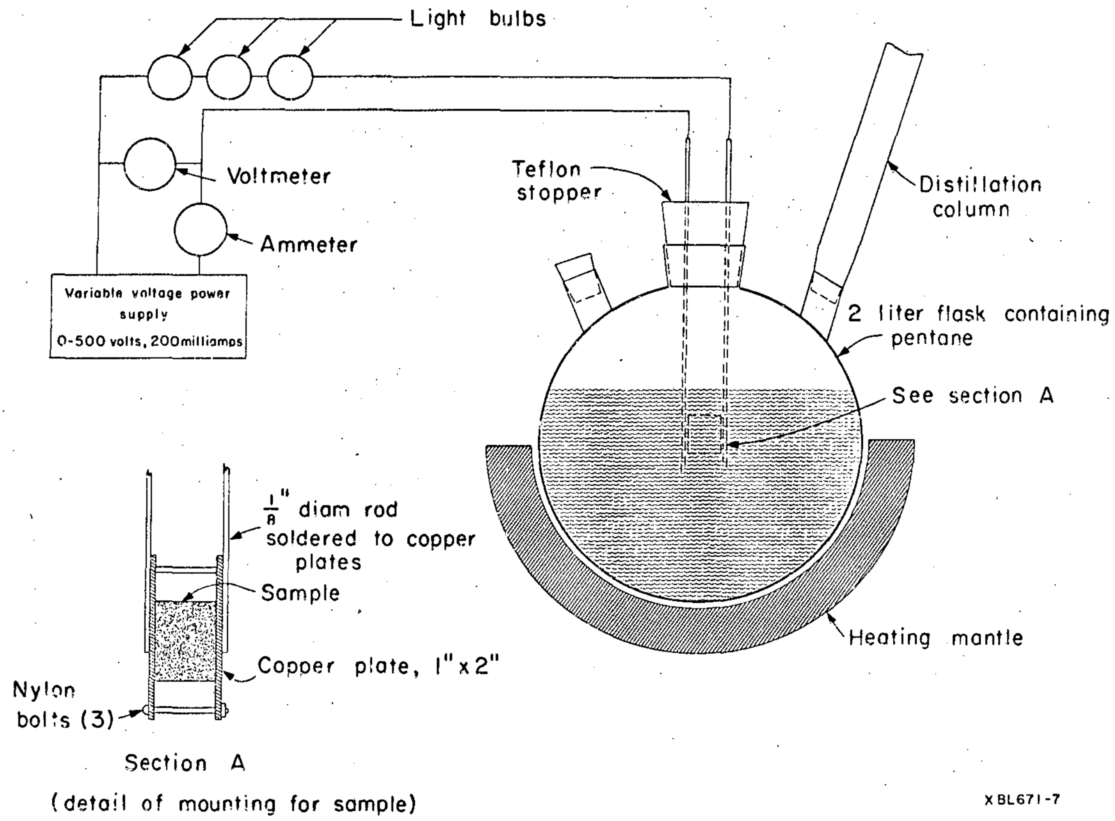

Fig. 2. Apparatus used for drifting lithium into germanium. The light bulbs were used as high impedance resistors to avoid large current surges through the sample if the sample should become conducting.