

THE FABRICATION OF SEMICONDUCTOR DETECTORS

by

RAYMOND L. MARCOTTE

B. S., Lowell Technological Institute, 1962

A MASTER'S THESIS

submitted in partial fulfillment of the
requirements for the degree

MASTER OF SCIENCE

Department of Physics

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1965

Approved by:



Major Professor

LD
2008
T4
1965
M32
C.2
Document

TABLE OF CONTENTS

INTRODUCTION 1
THEORY..... 2
EXPERIMENTAL PROCEDURE.....14
DISCUSSION AND EXPERIMENTAL RESULTS.....28
CONCLUSION,.....48
ACKNOWLEDGEMENTS.....49
LITERATURE CITED.....50

INTRODUCTION

Over the past four or five years the development of semiconductor detectors has revolutionized experimental work with charged particles in nuclear spectroscopy. More recent developments, using germanium, have given very encouraging results with gamma rays. The possibilities of semiconductor detectors were first demonstrated in 1949 by McKay who used a grown p-n junction to detect alpha particles. This diode had poor energy resolution and a very small effective area since the particles were incident parallel to the plane of the junction. (11) Intensive development of semiconductor detectors was delayed until 1958 due to the lack of satisfactory semiconductor materials.

Three main types of detectors have been fabricated to date: 1) the diffused p-n junction detector; 2) the surface barrier detector; and 3) the p-i-n detector. There has been some study of a fourth type, the bulk conductivity counter. (9) Although all three types may be obtained commercially, there are several advantages for one to be able to fabricate these detectors himself. The detectors can be made for a fraction of the cost of commercially made detectors. Also one is able to fabricate detectors for special applications which would not be available commercially.

Although the diffused p-n junction and the surface barrier detectors are very similar in theory, their method of fabrication is extremely different. In this research, work was done on the fabrication of the diffused p-n junction detector and the p-i-n detector. The reader is referred to N. J. Hansen's article (4) and literature cited therein for fabrication procedures for the surface barrier detector.

THEORY

A p-n junction is defined as that region which exists between n-type semiconductor material and p-type material when the two types are present in a single crystal. When a p-n junction is first formed, the two conduction bands are at the same energy level. As conduction electrons are more numerous in the conduction band of the n-type material there is a diffusion current of electrons from the n to p type material across the junction. Thus the p-type material acquires a negative charge and the n-type material becomes positively charged because it now contains a number of ionized donors whose charges are not balanced by an equal number of free electrons. A similar process occurs in the valence band. There is a diffusion current of holes moving from the p to n type material leaving behind a number of ionized acceptors which produces a negative charge in the p-type material near the junction. Thus a contact potential difference develops across the junction in such a direction as to oppose the further flow of majority carriers. A new equilibrium is established in which the contact potential difference is just large enough to counteract the tendency for more majority charges to flow across the junction in consequence of the concentration gradients of such carriers in and near the junction. The equilibrium condition is reached when the Fermi level is at the same height on both sides of the junction. (15)

There are a few holes on the n-side of the junction and a few electrons on the p-side of the junction. These minority carriers are subject to diffusion and continuously wander toward the junction. After a time they come under the influence of the built in electric field and eventually cross the junction. At equilibrium the flow of minority carriers is balanced by an equal flow of majority carriers due to carriers which have enough energy to cross the barrier against the built-in

field. (17)

If now a reverse bias is applied to the diode, the applied voltage will aid the built-in voltage and the barrier height will increase. The applied field will tend to pull the majority carriers away from the barrier, thus extending the space charge layer. The resistivity of the space charge layer will be high since there is a low concentration of carriers within this region and practically all the applied potential will appear across the charge-depletion layer. (16) It is in the depletion layer that the conditions for detector operation can exist. Under the application of a reverse bias the current noise generated in the depletion layer is reduced since the free majority carrier populations are reduced below their thermal equilibrium numbers and consequently the current component due to the flow of majority carriers will be reduced.

The theory discussed above is applicable to the diffused p-n junction detector, which is usually formed by a shallow diffusion of phosphorous into high resistivity p-type silicon forming a p-n junction very close to the surface. The fabrication techniques will be discussed later.

Charged particles incident upon a semiconductor produce hole-electron pairs by inelastic collisions. For a p-n junction detector under reverse bias, carriers created in the depletion zone will be swept across the depletion layer by the applied field and collected as a voltage pulse since the space charge region is, in effect, a parallel plate capacitor with a dielectric between the plates. The distance between the plates is the width of the barrier.

Electrons or holes created outside the depletion region must first diffuse to that region before they can add to the signal. In general, it takes longer to collect charge by diffusion than by drift. If the diffusion times are longer than the RC time constant of the junction

and associated circuits the pulse height will no longer represent the energy lost by the particle. (8) Thus it is very important that the depletion region be greater than the range of the particle to be detected in order that linearity with energy be preserved.

The charge released by the incident particle is closely proportional to the energy absorbed within the sensitive zone and has been found to be independent of the nature of the particle. In silicon it is found that it takes, on the average, 3.5 ev to produce an electron-hole pair. Thus any charged particle losing E mev of energy in the sensitive region will produce N pairs of carriers, where N is given by:

$$N = (E/3.5) \times 10^6 \quad (1) (13)$$

The total charge that the carriers will liberate is given by

$$Q_L = 1.6N \times 10^{-19} \text{ coulombs} \quad (2) (13)$$

If we assume that all the charge released is collected then the pulse height P is given by $P=Q_L/C$, where C is the capacitance of the detector plus the input capacitance of the amplifier used. If, however, the carriers only traverse a fraction f of the total sensitive zone, then the pulse height will be given by $P=fQ_L/C$. (13) Since, as will be shown shortly, the capacitance of a detector varies with applied bias, the pulse height will also vary with applied bias. This however, can be eliminated by the use of a charge sensitive preamplifier.

For good proportionality it is also essential that the "window" thickness be negligible. The window is the highly doped n-type layer between the surface of the detector and the depletion zone. Holes generated in this region would be expected to have very little chance of reaching the sensitive zone and being collected. The reason for this is partly due to the negligible electric field in this region but mainly due to heavy trapping and very short carrier lifetimes because of the intense doping in this region. Thus the reduction of the window to a minimum is essential

for good linearity of pulse height versus energy and for detection of low energy particles.

It was stated previously that for good proportionality between energy and charge released it is essential that all the charge be created in the sensitive region. Thus the thickness of the depletion layer sets an upper limit on the energy which may be measured. The width of the depletion layer can be calculated from a solution of Poisson's equation. For the p-type region this is given by:

$$\partial^2 V / \partial x^2 = (4\pi q/k) (N_A + n-p) \quad (3)$$

where N_A is the acceptor impurity concentration, n and p are the local electron and hole densities and k is the dielectric constant of the crystal.

Although an exact solution is quite involved, we can make some approximations which reduce the calculation considerably. We assume that throughout the depletion layer n and p are small compared with N_A . We also assume that the junction is abrupt, the barrier has abrupt edges and the impurity concentrations are constant in the p and n regions. Making these approximations one obtains for the width X of the depletion zone:

$$X = (kV/2\pi q)^{1/2} [(N_A + N_D)/N_A N_D]^{1/2} \quad (4) \quad (19)$$

where V is the reverse bias. For most cases in practice, it happens that the impurity concentrations on both sides of the junction differ greatly.

For the phosphorous diffused type, $N_D \gg N_A$ and the width is given by:

$$X = (kV/2\pi q N_A)^{1/2} = (k\mu_p \rho V/2\pi)^{1/2} = 3.2 \times 10^{-5} (\rho V)^{1/2} \text{ cm.} \quad (5)$$

where μ_p is the hole mobility and ρ is the resistivity in ohm-cm. Thus the depletion layer lies almost entirely in the p-type region. (2)

The capacitance of the reversed biased junction will be approximately that of a plane parallel capacitor of thickness X with a silicon dielectric. For the junction is, in effect, a layer of high resistivity material

separating opposite layers of electric charges. The capacitance is given by:

$$C = kA/4\pi X \quad (6)$$

where A is the area of the junction. Using equation 5 in equation 6 gives for the capacitance:

$$C = A(k/8\pi\mu_p\rho V)^{1/2} \quad (7)$$

Thus it can be seen that large depletion layers, obtained by increasing the ρV product, will decrease the capacitance and increase the voltage pulse height output, giving a better signal-to-noise ratio. (2)

The reverse current in a detector can be the main source of noise in the system and may very well limit energy resolution. There are three components of the total reverse current: (1) the drift current; 2) the carrier generation current; and 3) the surface leakage current.

The drift current has two components, one due to diffusion of holes from the n side of the junction into the depletion layer and the other due to diffusion of electrons from the p side. In p-n junction detectors, one side of the junction is extremely shallow and it is assumed that no appreciable drift current can originate therein. (18)

The carrier generation current also has two components arising from carriers produced by thermal generation on both sides of the junction. Again the component from the thin surface layer is thought to be negligible. In general, the carrier generation current exceeds the drift current by an order of magnitude or more in a junction counter. (18)

The surface leakage current is mathematically unsolvable and presents a very serious problem in practice. It appears that even with good surface conditions, the surface leakage current is an order of magnitude or more greater than the carrier generation current.

McKenzie and Waugh (12) have found for a p-n junction in a high

resistivity p-type crystal that the total reverse current at ambient temperatures is given by:

$$I = 1.7 \times 10^{-2} \frac{\rho}{\tau^{1/2}} \sqrt{38} \frac{\rho^{1/2} V^{1/2}}{\tau} \text{ mA/cm}^2 \quad (8)$$

where ρ is in ohm-cm., V in volts and τ , the carrier lifetime, in microsec. Thus it is seen that long carrier lifetime is essential for low reverse current. Recalling the relation for depletion layer thickness and the relation for reverse current, one can see that optimization of the ρV product is essential for a good detector.

The major limitation of p-n junction detectors is the relatively thin depletion region that can be achieved. The inability to produce depletion thicknesses in excess of lmm led to the extension of Pell's lithium ion drift technique to fabricate the p-i-n detector with depletion layer thicknesses up to 5 mm.

The behavior of lithium in silicon was determined experimentally by Pell in 1960. (14) Lithium is an interstitial donor in p-type semiconductors with an ionization energy of 0.03 ev. It is assumed that the acceptor concentration in the p-type silicon is distributed uniformly throughout the silicon to a level of N_A acceptors/cc. Lithium is diffused into one side of the slice with a surface concentration of N_0 donors/cc, where $N_0 \gg N_A$, until a p-n junction is formed internally at $x=c$. The initial donor concentration as a function of the distance x from the surface is shown in Figure 1;

If a reverse bias is now applied to the n-p junction formed, an electric field (E) will be present in the space charge region extending a short distance on both sides of the junction. The electric field will cause the positively charged lithium ions to move from the lithium doped n-type region toward the p-type region. As drift continues, the Li^+ concentration at $x < c$ will decrease and the Li^+ concentration at

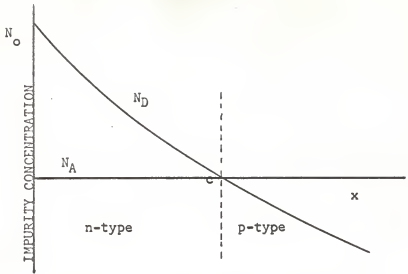


Figure 1. Initial Impurity Distribution

$x > c$ will increase. The value of N_D will tend toward N_A for $x < c$ and rise toward N_A at $x > c$ thereby producing an intrinsic semiconductor region and extending the region in which the driving field E is present. The impurity distribution is then given by Figure 2. The lithium concentration cannot, however, fall below N_A at $x < c$ and cannot rise above N_A at $x > c$ for this would change the space charge in such a way to make the Li^+ ions drift back to the form of Figure 2.

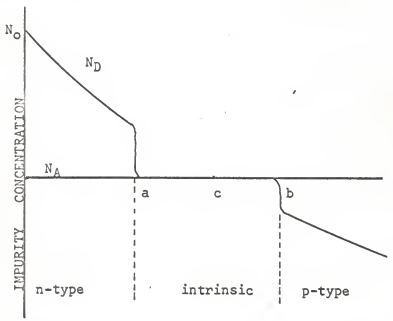


Figure 2. Impurity Distribution after drift

The process of ion drift results in a layer of crystal which becomes intrinsic due to compensation of the acceptor ions, usually boron, by the lithium donor ions. Though the intrinsic region may apparently be made as large as desired, it is limited by the effects of the carrier generation current that is present during drift due to the reverse bias and elevated temperatures that must be used. In a perfectly intrinsic region the electric field in this region would be constant as in Figure 3a. There would be no net space charge in this region due to perfect compensation. At elevated temperatures, the space charge due to the bulk reverse current is of sufficient magnitude to perturb the electric field in the intrinsic region as in Figure 3b.

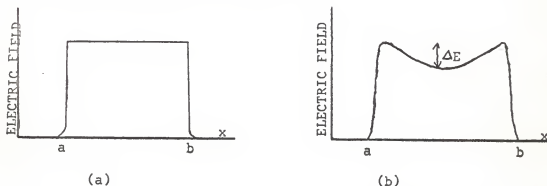


Figure 3. (a) The spatial distribution of the electric field in a p-i-n junction. (b) The perturbation of the electric field by the space charge of mobile carriers.

Mayer (10) has calculated the magnitude of the maximum drop in the field distribution ΔE as

$$\Delta E = \pi q n_i W^3 / 2k\tau\mu V \quad (9)$$

where n_i is the intrinsic carrier concentration, W is the width of the intrinsic region, τ the carrier lifetime, and μ the carrier mobility. Therefore as the width of the intrinsic region increases the perturbation of the electric field will increase. As a consequence of the field distortion, the ion-drift process will redistribute the lithium ions until they com-

compensate for the space charge of the mobile carriers, producing the resultant impurity distribution given in Figure 4.

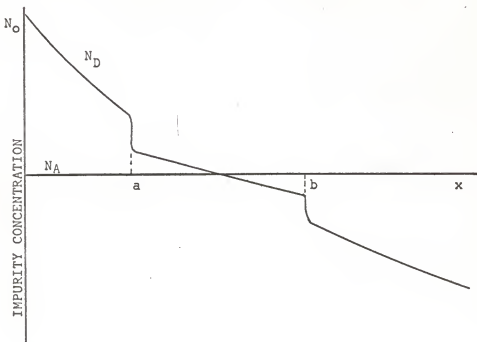


Figure 4. Impurity distribution in a deep intrinsic zone.

This problem can be overcome to a certain extent by completing the drift at a lower temperature, thereby reducing the number of carriers thermally generated and decreasing the space charge on both sides of the junction. The extent of compensation in the drifted region has been calculated by Lehrer and Reiss. (6) Pell has found that for long drift times the width of the drifted region is given by:

$$W = (2\mu Vt)^{1/2} + \text{const.} \quad (10)$$

where μ is the mobility of the donor ion, V is the voltage applied during drift, and t is the time of drift. (14)

In a p-i-n detector the sensitive zone is primarily determined by the width of the so-called intrinsic region and therefore is nearly constant because the space-charge regions on both sides of the intrinsic region will be small compared with the intrinsic region and will not change appreciably with applied voltage. At any reverse bias the width of the sensitive zone can be calculated from

$$C = kA/4\pi W \quad (11)$$

where C is the junction capacitance. The reverse current at high bias has a large contribution from surface leakage, but in detectors with deep depletion layers at low bias the carrier generation and drift currents are dominant. The reverse current for the p-i-n structure has been found to be

$$I = q(n_i^2/N_A)(D/\tau)^{1/2} + qn_i W/2\tau \quad (12)$$

where D is the diffusion constant. (10) For deep depletion layers the carrier generation current, the second term in equation 12, is usually dominant.

If one assumes a constant electric field across the sensitive zone, the collecting time of the carriers produced by incident radiation can be calculated to be

$$t_c = \frac{W^2}{\mu V} \quad (13)$$

and can be seen to be strongly dependent on reverse bias. Collection time, however, is found to be better than would be expected from the above calculation because the carriers under collection probably have longer lifetimes than those calculated from the reverse current and consequently have higher mobilities.

The major disadvantages of the ion-drift method are that the lithium diffusion is deep and leaves a highly pitted surface, so that the window thickness is large due to the highly doped n-type layer and is non-uniform. Also the lithium continues to diffuse from the n-type region into the depletion layer at room temperature thereby decreasing the intrinsic region and increasing the capacitance of the device. This effect can be prevented by storing the device with a small bias applied or by placing them under a small bias for a period of time until the capacitance regains its original value. Surface pitting can be eliminated by using evaporated

lithium instead of the more commonly used lithium-in-oil suspension, but there is still the problem of the large window thickness. The window may be reduced by the standard procedure of drifting the lithium through the slice to the back contact, usually gold or nickel, providing the slice is not too thick. Thicknesses of depletion layers up to 5 mm have been reported by Mayer. (9)

The electrical properties of a nearly intrinsic semiconductor useable as a radiation detector are determined by a very small concentration of impurity atoms and crystalline defects. For this reason semiconductor detectors are very susceptible to radiation damage. The effects of ionization, that is the displacement of electrons from their initial energy states in the lattice, has already been discussed. Ionization effects disappear very rapidly by recombination of carriers either at the boundary electrodes or at recombination centers within the crystal. However, it is possible that the incident radiation may displace atoms from their normal sites in the lattice leaving vacancies and interstitial atoms in the lattice. These crystal defects bring about a reduction in carrier lifetime and may also affect the resistivity of the crystal. The reduction in lifetime caused by radiation is first noticed by an increase in the reverse current, which causes an increase in noise, and then by a loss of resolution due to incomplete collection of carriers. The change in resistivity arises because nuclear transmutation of the silicon atoms produces atoms which may act as donors or acceptors thereby compensating the impurities already present. Prolonged irradiation may even cause a conversion to high resistivity material of opposite type. These radiation effects are not of consequence in most measurements where the flux of radiation is at a low level but they are important if the detector is to be used in high fluxes.

Klingensmith has shown that deterioration in alpha particle resolution

occurred after irradiation with 5×10^{11} fast neutrons/cm². Radiation flux greater than the above figure resulted in multiple peaking. (5)

It has also been observed that irradiation with alpha particles caused deterioration at a flux of 10^9 - 10^{11} alphas/cm². (20)

The main problem, as indicated in the fabrication of detectors, is to keep the noise level to a minimum. This means that the reverse current must be kept to a minimum. In practice, this means that the edge surface of the detector must be free from any contamination to reduce the surface leakage current and thereby reduce the noise. The bulk reverse current will depend upon one's choice of the resistivity, carrier lifetime, and geometry of the starting material.

EXPERIMENTAL PROCEDURE

The fabrication of semiconductor detectors is still somewhat of an art. Techniques which give good results for one experimenter are not guaranteed to give good results for another. Therefore it is mandatory to explore all techniques applicable to the manufacture of semiconductor detectors and develop a technique which gives the desired results. The techniques to be discussed here are those used in this work. However, some mention will be made of variations of these techniques used by other experimenters.

After the desired characteristics of the silicon were chosen, it was necessary to slice and lap the semiconductor. The slicing in this work was done by the manufacturer, Monsanto Chemical Company. At least 0.005 in. was lapped from each side of a slice to remove any damaged layers that may have resulted from the slicing operation. The slices were first hand ground on Buehler Limited Automet grinding papers. They were successively ground on numbers 240, 320, 400, and 600 grinding papers. Ten to fifteen minutes on each paper was usually sufficient to remove 0.005 in. from each side as measured by a micrometer.

In initial trials, the next step in the lapping procedure was to lap the slices on a rotating polishing wheel at a speed of 400-500 rpm with Buehler limited AB fine grinding compound (13 μ) on AB microcloth for about two hours or until all scratches, introduced by the 600 paper, had disappeared. Next an extra fine grinding compound (6 μ) was also used on AB microcloth until a highly polished surface was achieved. This step usually took one to two hours. The slice was held to a lucite holder with black apiezon wax and the sample was rotated by hand in the opposite direction to that of the polishing wheel. Using this procedure sometimes caused uneven lapping of the slice due to the inability to keep the slice perfectly flat on the polishing wheel. Consequently, the above procedure

was replaced by hand lapping on a glass plate with 20 μ , 13 μ , and 6 μ abrasive powders. This did not produce a high polish on the slice but it was found subsequent etching produced that finish. In between each step the abrasive powder was removed by ultrasonic agitation in distilled water for one minute. Failure to remove all abrasive powder from the slice prior to etching resulted in a speckled surface after etching.

After the final lap the slices were cleaned thoroughly in trichloroethylene and then in ethyl alcohol. Then the slices were soaked for five minutes in hot (approximately 80°C.) HNO₃ and rinsed in distilled water. The slices were next soaked for 30 seconds to 1 minute in HF at room temperature. Each slice was etched at 5°C. for two minutes in CP-4 etch containing 5 parts HNO₃, 3 parts HF, and 3 parts HC₂H₃O₂(by volume). At the end of two minutes, the etchant was diluted and decanted with distilled water until no trace of etchant remained. The slices were removed from the water, rinsed in ethyl alcohol and wiped dry with either Kleenex or Kim-wipes.

For the phosphorus diffused p-n junction detector, there are two methods which one may follow. The first method tried was the "paint-on" technique. A phosphorous pentoxide solution was painted on one side of the lapped and etched slice. The P₂O₅ solution was made by dissolving 2 grams of P₂O₅ into 25cc of ethylene glycol. There was a rather violent reaction in which the solution turned black. A less violent reaction was observed when the solution was mixed at 5°C. The coated slice was baked at 100°C. for 1/2 to 1 hour to dry the surface coating. The temperature of the oven was then increased to 950°C and maintained at that temperature for 1/2 to 1 hour. At the end of this time the slice was slowly cooled at a rate less than 300°C per hour to room temperature so as to preserve the carrier lifetime. After the slice was cool, the side opposite to that on which the P₂O₅ solution was painted, was lapped

slightly for identification. The glass layer formed from the reaction of P_2O_5 with Si was then removed by soaking in HF for 30 seconds to one minute followed by a rinse in distilled water. The back of the slice was then lapped with 6 μ abrasive powder on a glass plate followed by ultrasonic agitation prior to making an electrical contact.

The diffused side of the slice was masked with thermosetting adhesive tape and allowed to bake for 10 minutes at 95°C to set the tape. A Nickel contact was plated on the lapped face by an electroless nickel plating solution made from a mixture of 30 grams of Nickel Chloride, 10 grams Sodium Hypophosphate, 65 grams Ammonium Citrate, and 50 grams Ammonium chloride to one liter of distilled water. The solution, a bright green color, was filtered and stored in a polyethylene container until ready for use. Before using it, Ammonium Hydroxide was added until the solution turned a bright blue color indicating a pH value of 8-10. (21) The slice was soaked for two minutes in HNO_3 at room temperature and rinsed in distilled water. It was then dipped in HF for 15-30 seconds and transferred directly to the plating solution at 95°C. Four minutes in the plating solution was usually enough to insure a suitable deposition of nickel. Following a rinse in distilled water, the slice was placed in heated (approximately 70°C) trichloroethylene to remove the tape.

The slice was then cleaned thoroughly in trichloroethylene, ethyl alcohol, and wiped dry. Thermosetting adhesive tape or apiezon wax, either of which is acid resistant, was placed on both sides of the slice. The periphery of the slice was etched in 50% HNO_3 and 50% HF for seven to ten seconds at room temperature to remove the nickel. After cleaning in trichloroethylene and ethyl alcohol, the slice was placed in a dust free container for a day or more until ready for electrical testing.

The second method employed, that of gaseous diffusion of phosphorous, was carried out in the Lindberg multiple-zone furnace at Argonne National

Laboratory under the supervision of Harry M. Mann. A schematic diagram of the furnace used is given in Figure 5.

Prior to the diffusion, the inside of the furnace tube was cleaned with 50% HF and 50% HNO_3 solution. The tube was rinsed in distilled water and the outside of it was wiped with trichloroethylene. After insertion of the tube in the furnace, nitrogen gas was blown through the tube at 1 liter/minute to dry it. The remaining glassware was also etched in the 50 HF/50 HNO_3 solution for 5 minutes except for the pyrex boat which was etched for one minute and all were then rinsed in distilled water. The furnace temperature was increased to 100°C ., at which time the glassware was inserted in the furnace tube and the N_2 flow set at 1.5 liters/minute.

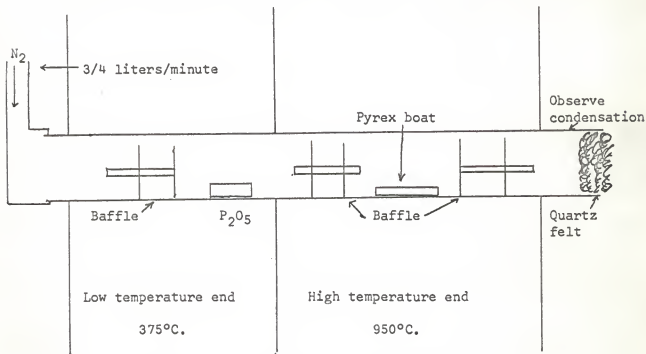


Figure 5. Furnace during phosphorous diffusion.

The system was then baked for 30 minutes with the low temperature end (LTE) at 400°C ., and the high temperature end (HTE) at 1050°C .. The temperature was then lowered to 100°C ., and the furnace was baked overnight with the N_2 flow at 0.5 liters/minute.

The next day the slices to be diffused were cleaned in ethyl alcohol

and wiped dry with Kimwipes. Any lint or dust particles were blown off with dry N_2 . The slices were placed on the pyrex boat which was inserted into the furnace tube with the LTE at 375° C. and the HTE at 950° C. The N_2 flow was set at 0.75 liters/minute. Phosphorous was diffused for fifteen minutes as measured from the instant that condensation appeared on the furnace tube as indicated in Figure 5. The boat was removed when the furnace had cooled to approximately 580°C. and placed in a dust free box. After the slice had cooled to room temperature, the nickel contact was applied in the same manner as indicated previously.

At this point in the procedure, the diode properties and the capacitance-voltage characteristics of the device were observed to check the rectifying characteristics and the width of the depletion region respectively. The reverse current should be less than 5 μ a at about 100 volts reverse bias. Reverse currents higher than this will create more noise than is desired with resultant reduction in energy resolution. Though re-etching the periphery may reduce the reverse current, the carrier lifetime may have been considerably reduced by the heating cycle.

Prior to mounting the detectors, edge protection was applied to the detector. Good diode characteristics should be observed, however, prior to application of edge protection. In this work good diode behavior was not observed for any of the slices diffused, consequently no edge protection was applied. Mr. H. M. Mann provided for edge protection by performing a mesa-type etch prior to application of Apiezon W black wax. The wax was applied with a brush immediately after rinsing the detector in trichloroethylene and allowed to harden before applying any voltage to the detector. (9)

The detectors were mounted by means of pressure contacts on both faces. An advantage of this method is that the slice can be removed for further treatments. A diagram of the holder used is given in Figure 6.

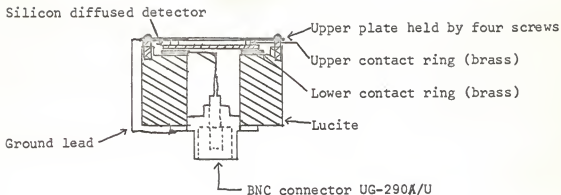


Figure 6. Holder for silicon diffused junction detectors.

The fabrication procedure for the lithium drift detectors was quite different from that of the phosphorous diffused detectors. Lithium, being an interstitial donor in p-type silicon, has a diffusion constant 10^5 to 10^7 higher than for impurities which diffuse by a substitutional process such as phosphorous. (10) Consequently, lower diffusion temperatures may be used, helping maintain carrier lifetime. The fabrication procedure used for the p-i-n detectors was almost identical to that used by H. M. Mann of Argonne National Laboratory.

Both faces of each slice were lapped with 20μ , 13μ , and 6μ abrasive powders on a glass plate. In addition to lapping both faces, the edge of the slice was lapped with 20μ abrasive powder until all damaged layers from the cutting operation were removed. Following ultrasonic agitation in distilled water, each slice was then cleaned in trichloroethylene, ethyl alcohol and distilled water. From this point on, the slice was handled only with stainless steel tweezers.

It was then placed in hot (80°C) HNO_3 for five minutes followed by a rinse in distilled water. After a 15 to 30 second soak in HF, the slice was transferred directly to either a gold or nickel plating solution. The nickel plating solution is the same as that discussed earlier. The use of nickel requires re-etching of the periphery after diffusion. The slice was plated for two minutes with the gold plating solution at 95° - 100°C . In transferring the slice from the HF to the plating solution, a small

amount of HF was carried along on top of the slice. Upon removal of the slice from the plating solution, it was rinsed thoroughly in distilled water. The gold plating solution had a concentration of 150 mg/cm^3 as obtained from the manufacturer. This was reduced to a concentration of 10 mg/cm^3 with distilled water and stored in a polyethylene container. Immediately before using this solution, it was mixed with acetic acid in the ratio of 1 to 1. Adherence of the gold layer was tested by rubbing the slice with a Kleenex.

Thermosetting adhesive tape was then applied to one face of the slice. The gold from the opposite face and periphery was removed by placing the slice in aqua regia for one minute and rinsing in distilled water. The opposite face was lapped to remove a few microns with 6 μ abrasive powder. The slice was then etched at 5°C in CP-4 etch. At the end of two minutes the etchant was diluted and decanted with distilled water. The tape was removed with trichloroethylene.

The all-glass vacuum heating apparatus, shown in Figure 7, was constructed for the lithium diffusion. A slice, which had been rinsed thoroughly in ethyl alcohol and wiped dry, was placed on the sample holder. A lithium in oil suspension was then applied to the upper surface by a rounded glass rod, taking care not to spill any on the edges. The vacuum system was sealed and evacuated overnight or until the pressure was approximately 5×10^{-6} mm. The sample was then heated to 340° to 350°C in five minutes and maintained at that temperature for 10 to 15 minutes. The system was allowed to cool to room temperature before the slice was removed from the system. The excess lithium on the diffused surface was removed by soaking in ethyl alcohol. Removal of the excess lithium by water was tried but resulted in more severe pitting of the slice than the alcohol.

Following a check on the diode characteristics, the drift process was begun. The reverse current should be less than $20 \mu\text{a}$ at 200 volts reverse

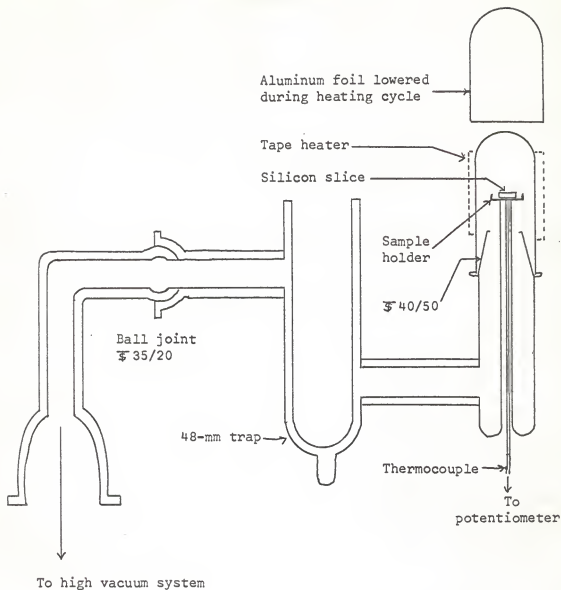


Figure 7. All-glass diffusion apparatus.

bias. The slices were drifted at 150°C and 300 volts reverse bias in Dow Corning type DC-710 silicone oil. The diffused slice was placed in the drift holder, shown in Figure 8, with its lithium side up. The spring clip held a nickel disk in contact with the diffused surface. The holder was placed in the bath and the slice was allowed to come to bath temperature with the voltage applied. The current during drift was not allowed to exceed 10 ma. The nomographs prepared by Blankenship (1) were used to calculate the drift times for various sensitive thicknesses. These nomographs are given in Plates I and II. Having known the voltage and

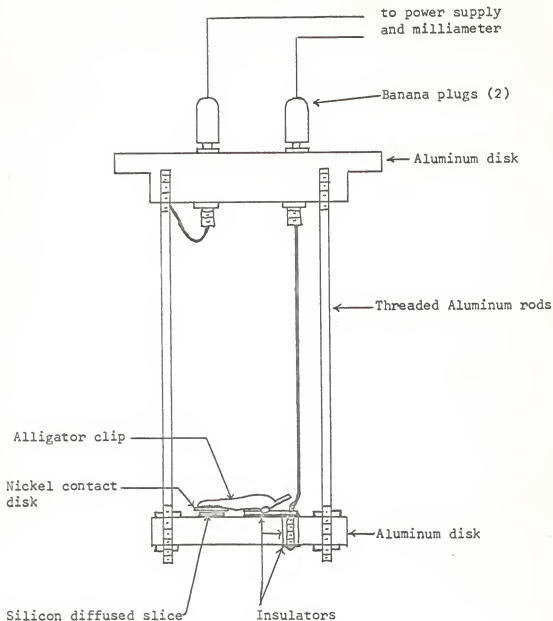


Figure 8. Drift Holder

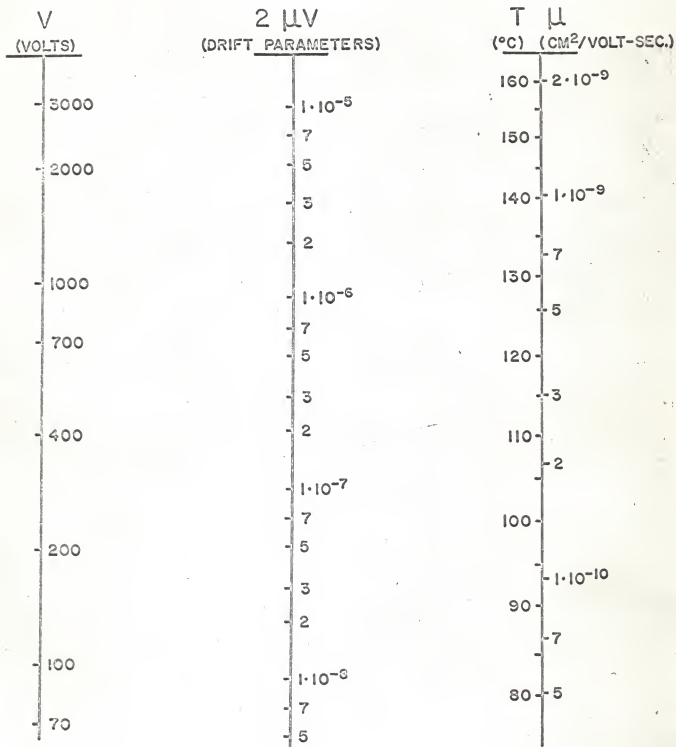
temperature, the drift parameter $2\mu\text{V}$ was solved graphically from Plate I. The drift time was then calculated from Plate II for the sensitive thickness desired. All detectors were drifted through the slice to the gold or nickel contact. Upon completion of drift the slice was removed from the drift holder, rinsed in trichloroethylene, ethyl alcohol and wiped dry.

The detectors were then mounted in a holder similar to the one used for the phosphorous diffused detectors. No edge protection was applied to any of the detectors. The detectors were then tested with internal

DESCRIPTION OF PLATE I

Lithium drift parameter nomograph

LITHIUM DRIFT PARAMETER NOMOGRAPH

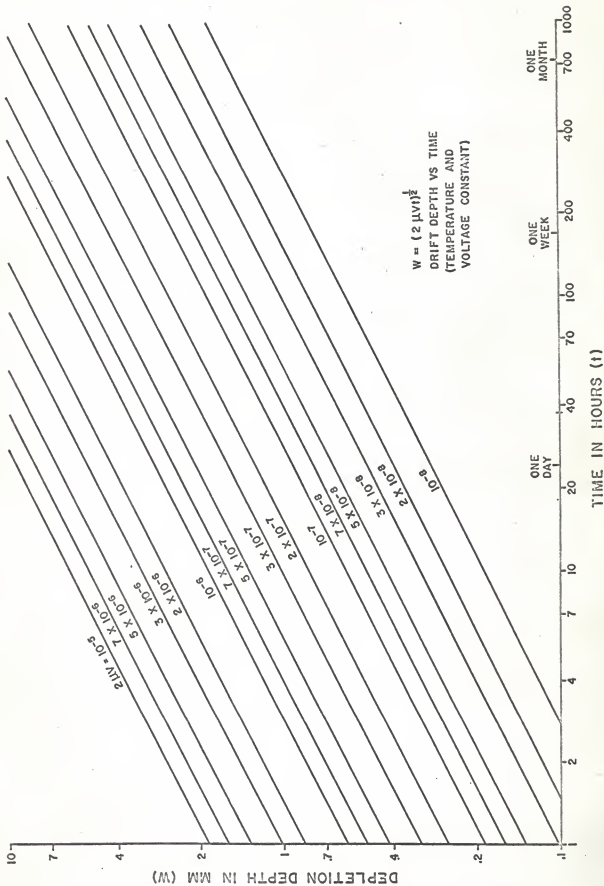


NOTE: DRIFT MOBILITY OF LI IONS IS GIVEN FOR SILICON WITH LOW OXYGEN CONCENTRATIONS.

DESCRIPTION OF PLATE II

Lithium drift depth as a function of time for various drift parameters ($2\mu\text{V}$).

PLATE II

UNCLASSIFIED
ORNL-LR-DWG-65740

conversion electrons from Bi²⁰⁷.

Blankenship (1) has developed a technique for achieving a thin dead layer on the n-side of the p-i-n diode. He performed a phosphorous diffusion at 1025°C for 2 hours. The phosphorous provided a layer with low sheet resistivity. He made an electrical contact on the opposite face by alloying aluminum. A controlled amount of lithium was evaporated onto the phosphorus diffused layer. An aluminum layer was then evaporated on top of the lithium. The slice was then heated to 400°C for 10 minutes and all of the lithium diffused into the slice. After cooling, the aluminum layer was removed. The lithium was drifted in the usual manner and dead layers of less than 7 microns thickness were achieved.

DISCUSSION AND EXPERIMENTAL RESULTS

Problems were encountered in almost all phases of preparation of the devices. One of the first problems was in the lapping procedure. While lapping on the AB microcloth with the 6 μ abrasive powder, the slices were scratched by contamination in the abrasive. This was finally traced to a plastic spoon which was used to mix the abrasive powder with distilled water. Use of a stainless steel spoon removed the contamination. It was also found that failure to remove all abrasive powder from the slice prior to etching resulted in a speckled surface. By examination of the slice under a microscope, one can see, whether or not all abrasive powder was removed from the slice prior to etching. It was observed that the etchant must be constantly stirred during etching. Failure to do this resulted in an uneven etched surface. The surface of the slice after etching should appear almost mirror smooth.

Silicon slices of 5000 ohm-cm resistivity, 1 mm thick, and 2 cm in diameter were used for the phosphorous diffused devices. Six slices were diffused by the "paint-on" technique. For the first two slices, the P₂O₅ solution was painted on by a cotton swab. This, however, proved to be an unsatisfactory technique in that it was extremely difficult to coat the slice evenly. The P₂O₅ solution was subsequently applied with an eye dropper which produced an even coating on the slice. All six slices prepared by this technique had whitish blotches on the phosphorous diffused side. This could have been possibly caused by some contamination left on the slice prior to diffusion, but the real cause of this problem was never found. Although these slices showed some rectifying properties, the reverse current in all the devices was never less than 5 μ a at 50v. This reverse current would have caused far too much noise than could be tolerated for detection of charged particles.

Two slices were prepared by gaseous phosphorous diffusion. Both slices were very sensitive to light but again had too much leakage current. The noise level in these slices was measured to be 150 millivolts peak to peak as measured at the output of the pre-amplifier at 0 volts reverse bias, decreased slightly up to 20 volts bias and increased considerably for voltages higher than 20 volts. Re-etching the periphery did not decrease the reverse current by any significant amount. It is believed that the leakage current was due to the bulk properties of the silicon slices. It is possible that the silicon was not pure enough for this work. Impurities in the silicon will produce recombination centers or traps which will reduce the carrier lifetimes considerably and therefore increase the reverse current. Further work on the phosphorous diffused devices was discontinued to work on the lithium drifted detectors.

Silicon slices of 100 ohm-cm, 3 to 5 mm thick, and 1 mm in diameter were used for the lithium drifted detectors. Nine slices were diffused with the lithium-in-oil suspension but only three, lithium #2,3 and 9, showed diode characteristics after diffusion. Some slices were diffused twice in an attempt to create a p-n junction. Lithium #2 and #3 were diffused for 15 minutes at 340°-350°C. Lithium #9 was diffused for 20 minutes at 340°C.

Lithium #2 was 4.62 mm thick. After diffusion the diode properties and capacitance-voltage characteristics were measured as shown in Table I. The slice was then drifted at 150°C and 300 volts for 60 hours. This

V_R	I_R	Capacitance
0 volts	0 μ a	23.0 pf
3	0.3	22.0
6	0.4	22.0
9	0.4	21.8
22 ¹ / ₂	0.5	21.6
67 ¹ / ₂	0.7	21.3
200	3.8	25.8

Table I

detector had a capacitance of 6.8 pf after drift at 0 volts reverse bias. The noise level of the device was 25 mv at 0 v, 35 mv at 50 v, 45 mv at 100 v, 60 mv at 150 v, and 80 mv at 200v. The response of this detector to internal conversion electrons from Bi^{207} is given in Plates III and IV. These plates show only the high energy electron peaks since the 480 and 553 Kev peaks did not appear in the spectrum. This indicated that there was still a thick window in the detector. It was placed back in the drift bath to redrift but this only caused the reverse current at room temperature to increase considerably. Failure to diffuse enough lithium into the slice to compensate for the full thickness of the device could cause this effect. No further drifting of this diode was attempted.

Lithium #3 had a thickness of 4.9 mm. The diode properties and capacitance-voltage characteristics, measured prior to drift, are shown in Table II. The diode was drifted for $72^{1/2}$ hours at 300 v and 150°C . The capacitance was then checked at room temperature and found to be 8 pf. The noise level was measured to be 35 mv at 0v reverse bias, 40 mv at 50 v, 50 mv at 100v, 60 mv at 150 v, and 80 mv at 200 v. The response of this detector at room temperature to internal conversion electrons from Bi^{207}

V_R	I_R	Capacitance
0 volts	0 μa	32 pf
3	0.3	31
6	0.4	31
$9^{1/2}$	0.4	31
$22^{1/2}$	0.5	30
$67^{1/2}$	0.7	28.8
200	4.5	32

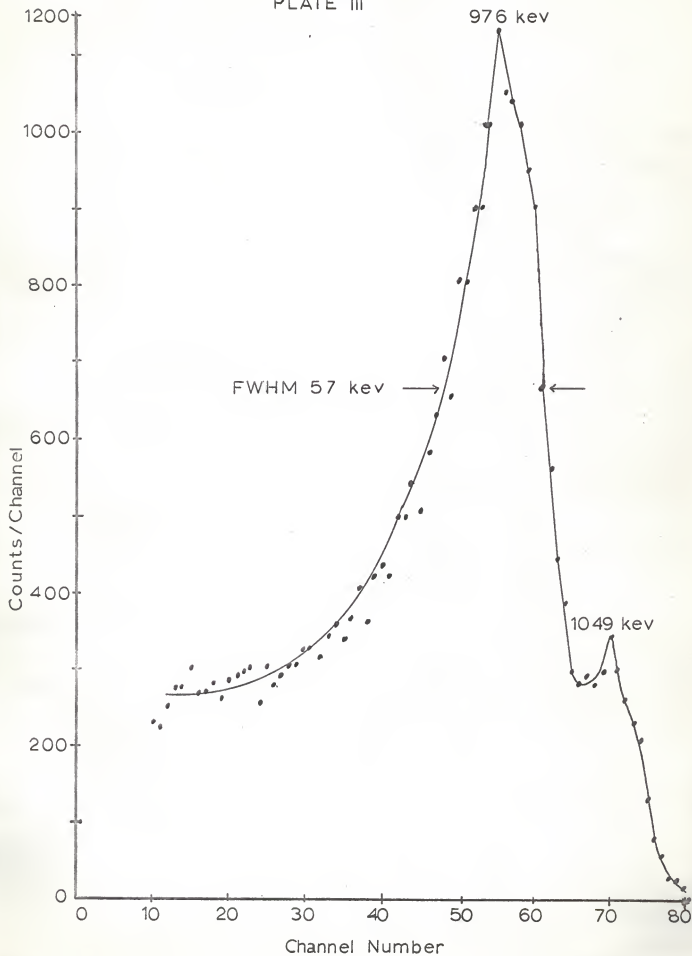
Table II

showed a resolution slightly less than 50 kev at full width at half maximum. When operated at 150 volts reverse bias, this diode gave 49.6 kev resolution for the 976 kev line from Bi^{207} as shown in Plate V. At 200 volts, the diode gave 47 kev resolution as shown in Plate VI for the 976 kev line.

DESCRIPTION OF PLATE III

Bi²⁰⁷; Lithium #2, cooled; 61 minutes; 200 v, 4, 4, 4, 1.4 v. The last five numbers in this description, and in the following descriptions, refer, in order, to the detector bias, the main amplifier gain setting, the post amplifier gain setting, the analyser gain setting, and the post amplifier bias setting.

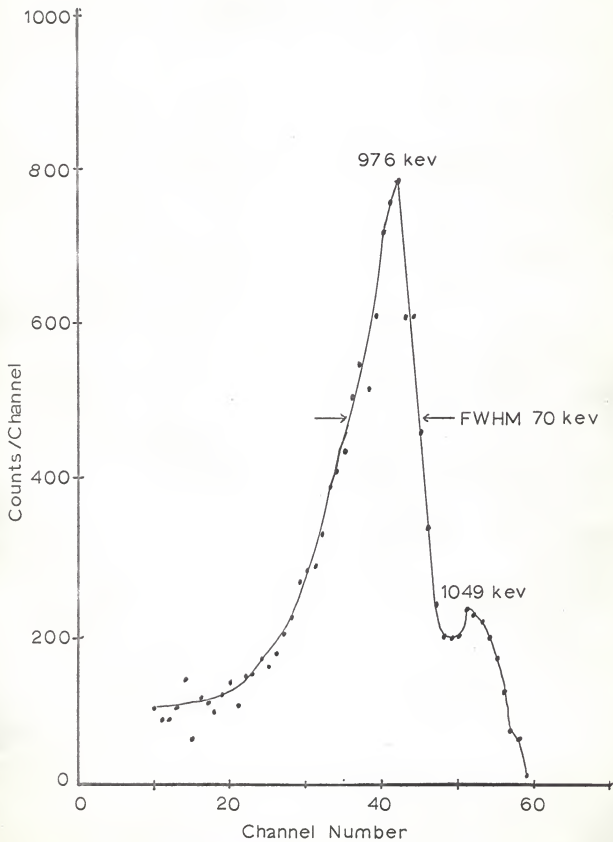
PLATE III



DESCRIPTION OF PLATE IV

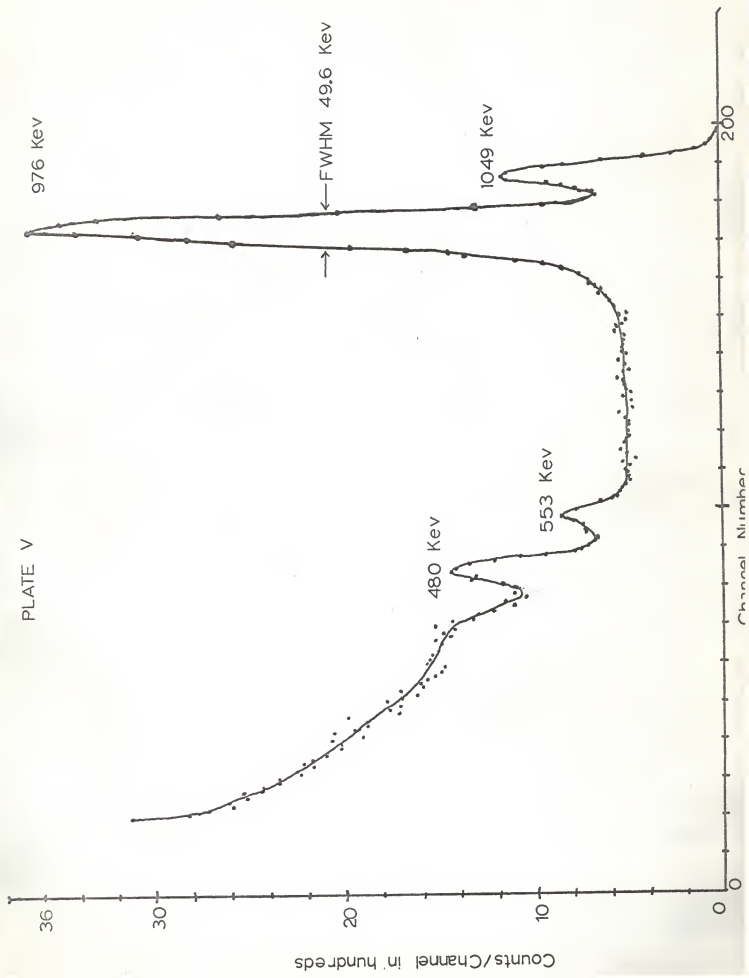
Bi²⁰⁷; Lithium #2, cooled; 40 minutes; 240 v, 4,4,
4, 1.4 v. A background spectrum has been subtracted.

PLATE IV



DESCRIPTION OF PLATE V

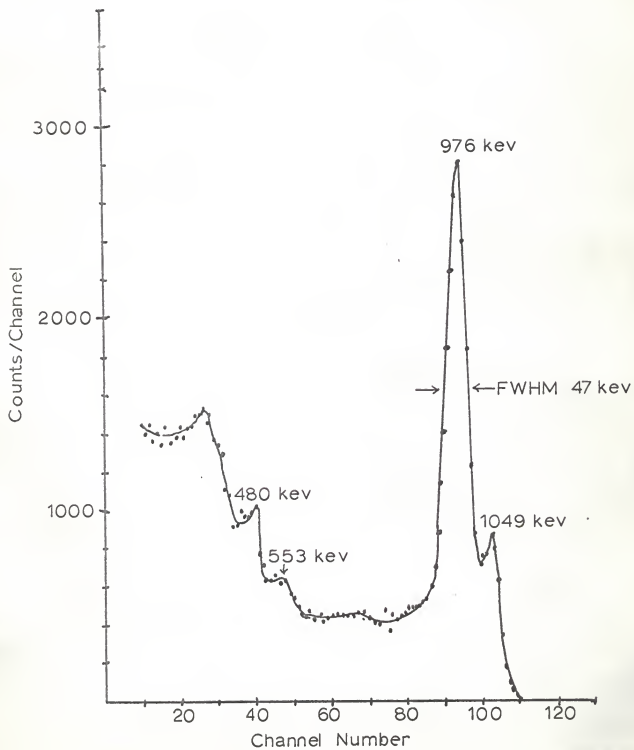
Bi²⁰⁷; Lithium #3; 23 minutes; 150 v, 4, 4, 3,
1.5 v.



DESCRIPTION OF PLATE VI

Bi²⁰⁷ ; Lithium #3; 12 minutes; 200 v, 2, 2, 7, 2.3 v.

PLATE VI



The detector was then redrifted for $2\frac{1}{4}$ hours but after this time the reverse current was much higher than before. It was decreased by drifting at a forward bias of 35v at 150°C for about $1\frac{1}{2}$ hours. The response to electrons from Bi^{207} after this drift is shown in Plates VII and VIII. The resolution deteriorated somewhat to 53-55 kev depending on the reverse bias. The long leading edge of the 976 kev line is apparently due to a thick window. Attempts to reduce the window by drifting only resulted in an increase in reverse current as before.

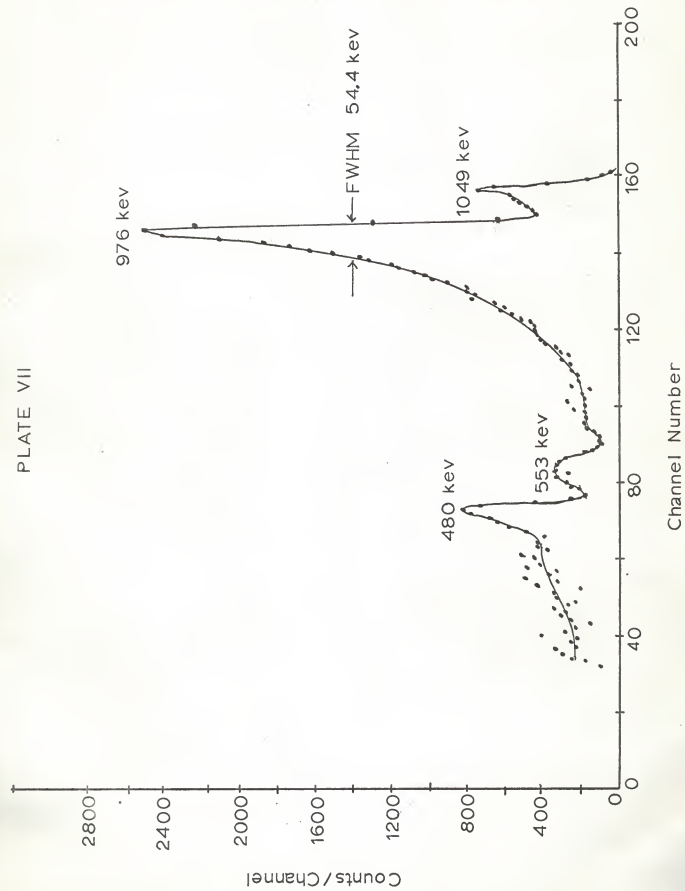
Lithium #9 was 4.8 mm thick. This diode did not show good diode properties after diffusion but after drifting for 3 hours the reverse current decreased to $<10\mu\text{a}$ at 200 v reverse bias. It was then drifted for 70 hours at 300 v and 150°C. The capacitance of the diode at 0 v bias was 13 pf. The noise level of the detector was 45 mv at 0 v reverse bias, 25 mv at 50 v, 30 mv at 100 v, 35 mv at 150 v, and 50 mv at 200 v. The response of this detector to Bi^{207} internal conversion electrons incident upon the nickel contact was extremely poor and the low energy electrons did not appear in the spectrum. Attempts to reduce the window by further drift only led to an increase in reverse current. However, the response to electrons incident upon the edge surface of the detector gave 34.4 kev resolution for the 976 kev line from Bi^{207} as shown in Plates IX and X.

207

DESCRIPTION OF PLATE VII

Bi ; Lithium #3, cooled; 100 minutes; 100 v, 4, 4,
4, 1.35 v. A background spectrum has been subtracted.

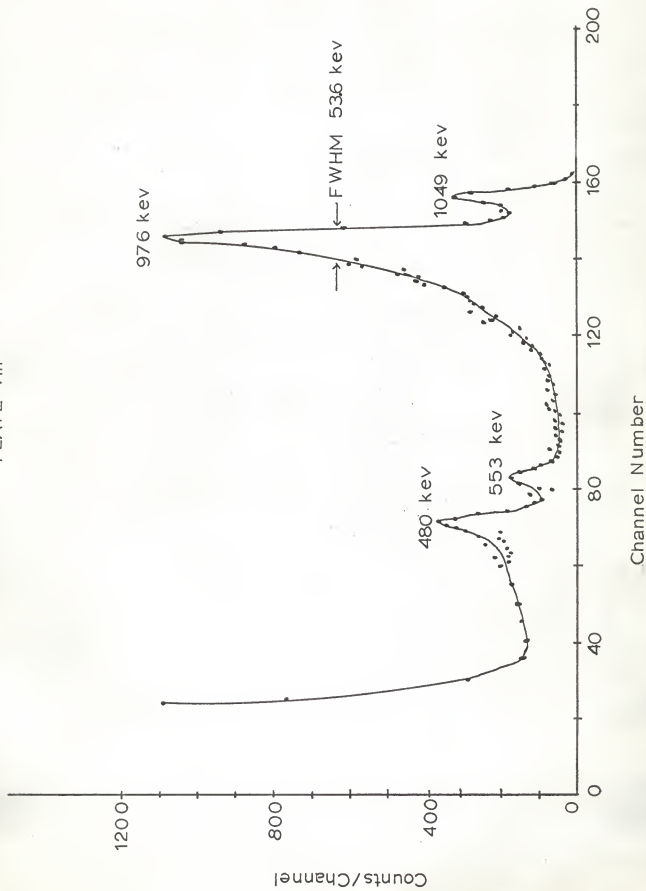
PLATE VII



DESCRIPTION OF PLATE VIII

Bi²⁰⁷; Lithium #3, cooled; 40 minutes; 150 v, 4, 4, 4, 1.55v.
A background spectrum has been subtracted.

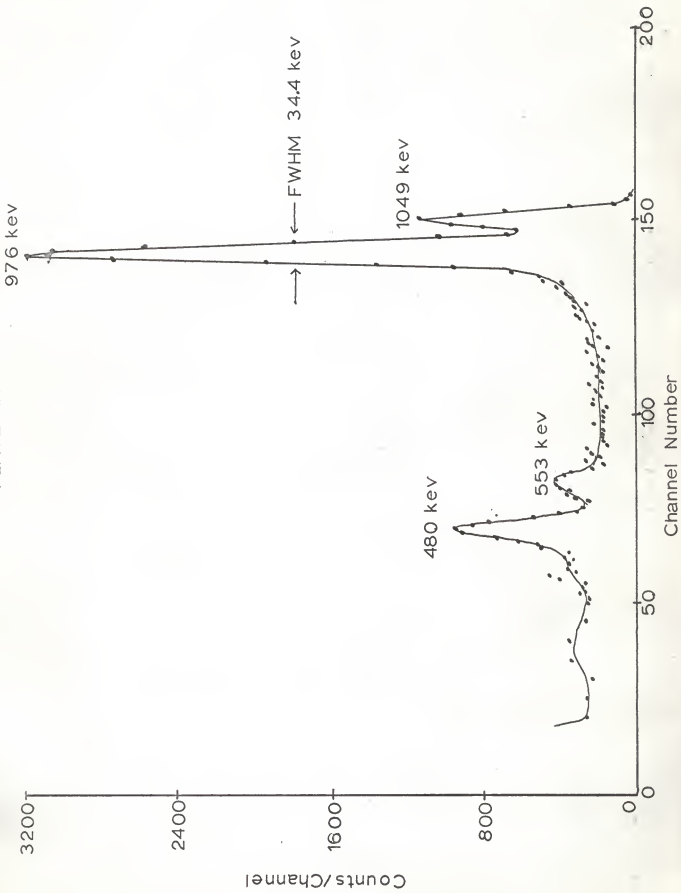
PLATE VIII



DESCRIPTION OF PLATE IX

²⁰⁷Bi ; Lithium #9; 100 minutes; 100 v, 4, 2, 7,
3.0 v. A background spectrum has been subtracted.

PLATE IX

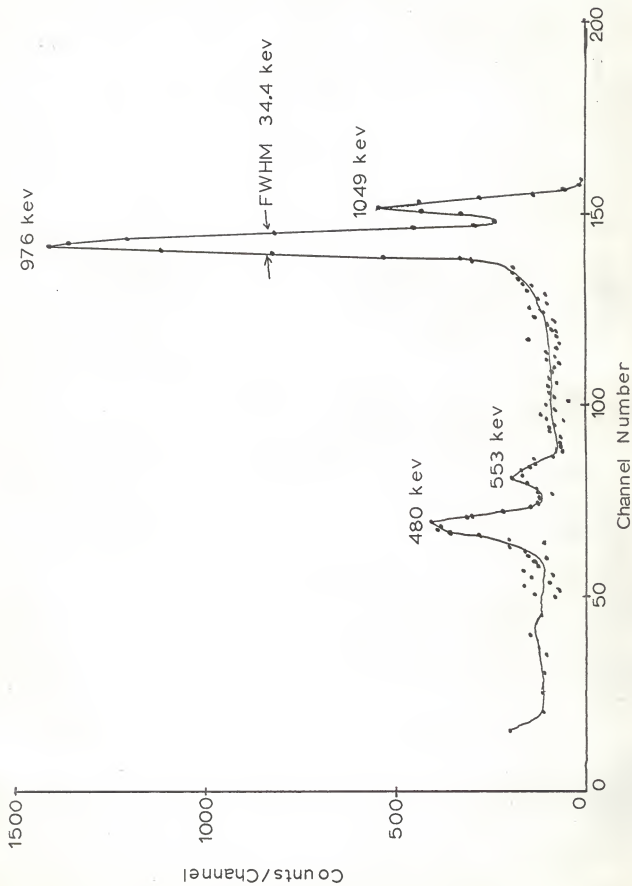


DESCRIPTION OF PLATE X

207

Bi²¹⁰; Lithium #9, 40 minutes; 150 v, 4, 2, 7,
3.0 v. A background spectrum has been subtracted.

PLATE X



CONCLUSION

Semiconductor detectors, in this work, were fabricated with fair results. No satisfactory phosphorous diffused detectors were made but it is believed that this was due to unsatisfactory silicon and not with the techniques employed. Fair results were obtained with the lithium drifted detectors. The problem of the large window thickness could be resolved by using thinner silicon slices which would permit drifting the lithium completely through the slice. No diode properties were obtained for the thin slices that were diffused in this work. Good resolution was obtained, however, for Lithium #9 with the electrons incident on the edge of the detector.

Once the problem of drifting completely through the slice is resolved, these techniques could be extended to germanium slices. The fabrication and use of germanium lithium drifted detectors for the detection of gamma rays would be extremely beneficial in nuclear physics research.

ACKNOWLEDGEMENTS

The author wishes to express his sincere thanks to Dr. Louis Ellsworth for his guidance and advice throughout this work, and to Dr. A. B. Cardwell for making the project possible. Sincere thanks and gratitude are also extended to Mr. Harry M. Mann for allowing the author to work with him for a week and to the Associated Mid-western Universities for financing the trip to Argonne National Laboratory.

LITERATURE CITED

1. Blankenship and Borkowski. Improved Techniques for Making P⁺-I-N⁺ Diode Detectors. IRE Trans. on N.S., Vol. 9, No. 3 (June, 1962), p. 181
2. Dearnaley and Northrop. Semiconductor Counters for Nuclear Radiations. London: Spon Limited, 1963. pp. 127-129
3. Ibid., pp. 265-288
4. Hansen, N. J.. Encapsulated Surface Barrier Detectors, Some Methods and Techniques. IRE Trans. on N.S., Vol. 9, No. 3 (June, 1962), p. 217
5. Klingensmith, R. W.. The Effect of a High Radiation Environment on Gold-Silicon Charged Particle Detectors. IRE Trans. on N. S., Vol. 8, No. 1 (Jan., 1961), p. 112
6. Lehrer and Reiss. Details of Ion Drift in an n-p Junction. Journal of Applied Physics, Vol. 33, No. 7 (July, 1962), p.2353
7. Mann, H. M.. private communication (April, 1964)
8. Mayer, J. W.. The Development of the Junction Detector. IRE Trans. on N.S., Vol. 7, No. 2-3 (June-Sept., 1960), p. 178
9. Mayer, J. W.. The "State-of-the-Art" in Nuclear Particle Detectors. IRE Trans. on N. S., Vol. 9, No. 3 (June, 1962), p. 124
10. Mayer, J. W.. Characteristics of p-i-n Junctions Produced by Ion-Drift Techniques in Silicon. Journal of Applied Physics, Vol. 33, No. 9 (Sept., 1962), p. 2894
11. McKay, K. G.. A Germanium Counter. Physical Review, Vol. 76, No. 10 (Nov., 1949), p. 1537
12. McKenzie and Waugh. Silicon Junctions as Particle Spectrometers. IRE Trans. on N. S., Vol. 7, No. 2-3 (June-Sept., 1960), p. 195
13. Miller, Brown, Donovan, and Mackintosh. Silicon p-n Junction Radiation Detectors. IRE Trans. on N. S., Vol. 7, no. 2-3 (June-Sept., 1960) p. 185
14. Pell, E. M.. Ion Drift in an n-p junction. Journal of Applied Physics, Vol. 31, No. 2 (Feb., 1960), p. 291
15. Shive, J. N.. The Properties, Physics, and Design of Semiconductor Devices. Princeton: D. Van Nostrand Company Inc., 1959. pp. 341-343
16. Ibid., pp. 350-351
17. Taylor, J. M.. Semiconductor Particle Detectors. Washington: Butterworths Inc., 1963. pp. 48-52
18. Ibid., pp. 71-75
19. Ibid., p. 168

20. Ibid., pp. 114-115
21. Transistor Technology, Vol. III, Edited by F. J. Biondi. Bell Labs Series. Princeton: D. Van Nostrand Company Inc., 1958 p. 173

THE FABRICATION OF SEMICONDUCTOR DETECTORS

by

RAYMOND L. MARCOTTE

B. S., Lowell Technological Institute, 1962

AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Physics

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1965

ABSTRACT

Semiconductor detectors were fabricated for use as electron detectors in the study of nuclear decay schemes. Phosphorous was diffused by the "paint-on" technique and gaseous diffusion into 5000 ohm-cm resistivity silicon slices. Although the diffused slices showed some rectifying properties and were light sensitive, the noise level in all the devices was much too high to be used as particle detectors. The noise level in all the devices was in excess of 100 mv. The large reverse current and noise was attributed to the bulk properties of the silicon. It was believed that the silicon was not pure enough to be used in this work and consequently the carrier lifetime was too short.

Lithium drifted detectors were fabricated from 100 ohm-cm resistivity silicon slices. Three detectors were fabricated by the diffusion of lithium into silicon in vacuum at 340°-350°C followed by drift in an electric field in a silicone oil bath. One such diode showed a resolution (full width at half maximum) of 57 kev from internal conversion electrons from Bi²⁰⁷ when cooled to 77°K. This diode had a window of greater than 200 microns. Attempts to drift the lithium further to reduce the window led to an increase in reverse current. One possible reason for this is that the lithium concentration was not great enough to compensate for the acceptor concentration in the p-type silicon. This effect occurred on all three detectors that were made. All three detectors had thicknesses greater than 4.62 mm.

The second detector had a window thickness less than 100 microns but the resolution was limited by noise in the detector. The response of this detector to internal conversion electrons from Bi²⁰⁷ gave slightly less than 50 kev resolution. The resolution was poor due to the large window and noise in the detector. The resolution did not improve when the

detector was cooled to liquid nitrogen temperature.

The third detector had a noise level of 35 mv at 150 v but the window thickness, which could not be made thinner by further drifting due to the increase in reverse current, was too large to resolve even the 976 and 1049 kev lines from Bi²⁰⁷ when the particles were incident upon the nickel contact. However, when the particles were incident upon the edge of the detector, it gave a resolution of 34.4 kev for the 976 kev line from Bi²⁰⁷. Resolution was limited by noise in the detector since there was essentially no window when the particles were incident in this direction.