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THE EFFECTS AND CONTROL OF SURFACE STATES DURING LITHIUM ION DRIFT IN SILICON

Robert P. Lothrop

November 1969

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This work is dedicated to all men who hold reason as an absolute; and, particularly, to those whose efforts have enriched the body of Man's knowledge.

The Author

THE EFFECTS AND CONTROL OF SURFACE STATES DURING LITHIUM ION DRIFT IN SILICON

Table of Contents

Part I Introduction

Part II The Nature of the Intrinsic Surface

Part III Evaluation of Surface State Effects

A. Sample Preparation

B. Sample Evaluation

Part IV Pre-drift Surface Treatment

Part V Surface State Control - During Drift - by Gas Mixtures

Part VI Surface State Control - During Drift - by Liquids

References

Appendices

Appendix 1. Guard Rings

Appendix 2. Copper Stain Procedure

THE EFFECTS AND CONTROL OF SURFACE STATES DURING LITHIUM ION DRIFT IN SILICON

Robert P. Lothrop

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Berkeley, California

November 1969

In any silicon detector, the room temperature voltage and current characteristics, for the detector taken as a whole, are dominated by surface effects. A simple form of such a totally depleted, lithium drifted,[1] silicon detector is:

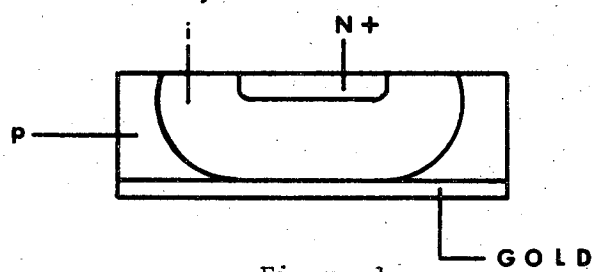
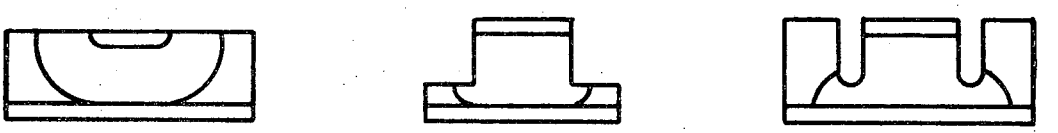


Figure 1.

The voltage and current characteristics of a completed detector having this structure are dependent on:

1. The last surface treatment and protection.
2. The ambient(s) and time of exposure thereto.
3. The nature of the intrinsic surface.
4. The quality of the gold surface barrier.
5. The quality of the silicon material.

If the fabrication process has these problems fully under control, then, in order of higher voltage and lower current characteristics, the sequence of detector geometries is:



A. Planar B. Top Hat C. Saw Cut

The reason that these characteristics improve in the order shown is that the field concentration along the intrinsic surface, which tends to "pinch-off" the surface channel, increases in the indicated order.[2] Note that in figure 2, B., the lithium drifted region must follow the surface around the right angle for the surface field concentration to be fully effective. Similarly, in figure 2, C., the advantage is lost if the lithium drifted region does not follow all the way around the curve of the "cut".

If the required result is extremely high voltage operation, independent of current, then the "double-drift"[3] geometry is the best choice:

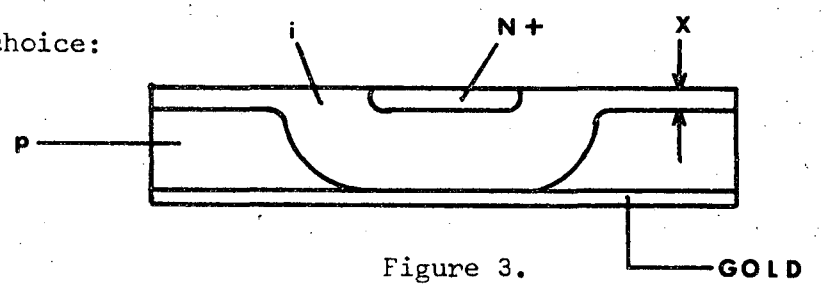


Figure 3.

In this detector geometry, the field concentration along the intrinsic surface is controlled to maximize the "pinch-off" effect

and thus use the surface states to full advantage. The thickness of the shelf region (x in figure 3.) is chosen to accomplish surface channel "pinch-off" at some small fraction of full detector voltage.

Further variations on these and other geometries may be made by the incorporation of a "guard ring"[4] structure. These variations are considered in Appendix 1.

An additional advantage of the geometries of figure 2, B. and C., over that of figure 2, A., is that very deep detectors may be fabricated on silicon materials in which the highest quality is limited to an area about the center of the crystal.

This work deals with the fact that the nature of the intrinsic surface, one of five primary factors in the total performance of a completed lithium drifted silicon detector, is determined by the ambient conditions during drift.

PART II

THE NATURE OF THE INTRINSIC SURFACE

The nature of the intrinsic surface is determined by the following factors:

A. Conditions of formation:

1. Length of the intrinsic surface as compared to the theoretical drift depth and as determined by the surface states.

2. Shape of the surface. Different shapes may change the effect of the conditions of drift and the characteristics of the completed device.

3. Accuracy of compensation.

   a) Uniformity along its length.

      (i) The effect of surface states.

      (ii) The effect of drift temperature.

   b) Uniformity perpendicular to the surface.

B. Conditions which bring about the preservation or destruction of the intrinsic surface after its formation:

1. Etching Effects: Some slow etches have been observed to increase the lithium concentration at the surface.

2. Diffusion Effects: The room temperature mobility of lithium ions is small but the concentration gradient is infinite going from N_a (the lithium concentration in the bulk) to zero abruptly.

3. Field Effects: Since the lithium ion mobility is real, the field due to the surface states and the voltages, "built-in" and/or applied, will effect the transport of lithium ions.

C. Quality of the Silicon:

The quality of the silicon used in the fabrication of these devices has been included as one of the five primary factors in the total performance of a completed detector. The bulk properties of the detector depend upon this quality. The nature of the intrinsic surface also depends upon this quality. Single crystal silicon quality is evaluated under the following categories:

1. Crystal perfection: Lineage, dislocation density, etc.
2. Uniformity of impurity distribution:
   a) Uniformity along the length.
   b) Uniformity along the radius.
3. Semiconductor properties: Type, resistivity, lifetime, etc.

The work to follow deals with the effects and control of the conditions of formation of the intrinsic surface, A, 1., above, and the evaluation thereof.

PART III

EVALUATION OF SURFACE STATE EFFECTS

A. Sample Preparation

The choice of pre-drift treatments and drift conditions, in terms of type, is a difficult one. However, an estimate of the effects of various pre-drift treatments and drift conditions can be made if one uses, as a guide, the electronic theory of acids and bases.[5] The theory must be considered in conjunction with the various classes of surface adsorption phenomena. The use of the electronic theory of acids and bases will facilitate the estimation of the type of most substances against the silicon surface. In general, Lewis acids are heavily p-type against silicon, and Lewis bases are heavily n-type against silicon. It is interesting to note that the benzene ring, considered to be an electron donor in organic chemistry, is an electron acceptor against silicon under drift conditions. The benzene ring is too p-type to be a useful drift medium.

Since the surface chemistry has a major influence on the lithium ion distribution, the use of lithium drift in silicon could be a powerful tool for the study of surface phenomena.

For the work presented here, all devices were given the pre-drift treatment(s) to be described in Part IV. All devices were then drifted in selected liquids or gas mixtures to be described in Parts V & VI.

Evaluation is then made after sectioning and copper staining to reveal the lithium distribution. The details of the copper stain procedure are given in Appendix 2.

B. Sample Evaluation

Considered below are eight cases which are examples of the two extremes obtainable by the selection of pre-drift treatments and drift conditions. These extremes are:

1. Intrinsic surface length short compared to the theoretical drift depth.

   a) Excessively p-type.

      Cases 1 and 2.

   b) n-type.

      Cases 3 and 4.

2. Intrinsic surface length approaching the theoretical drift depth.

   a) Lightly p-type

      Cases 5, 6, 7 and 8.

CASE 1 Top Hat Geometry - Excessively p-type Drift Conditions

Pictures 1 and 2

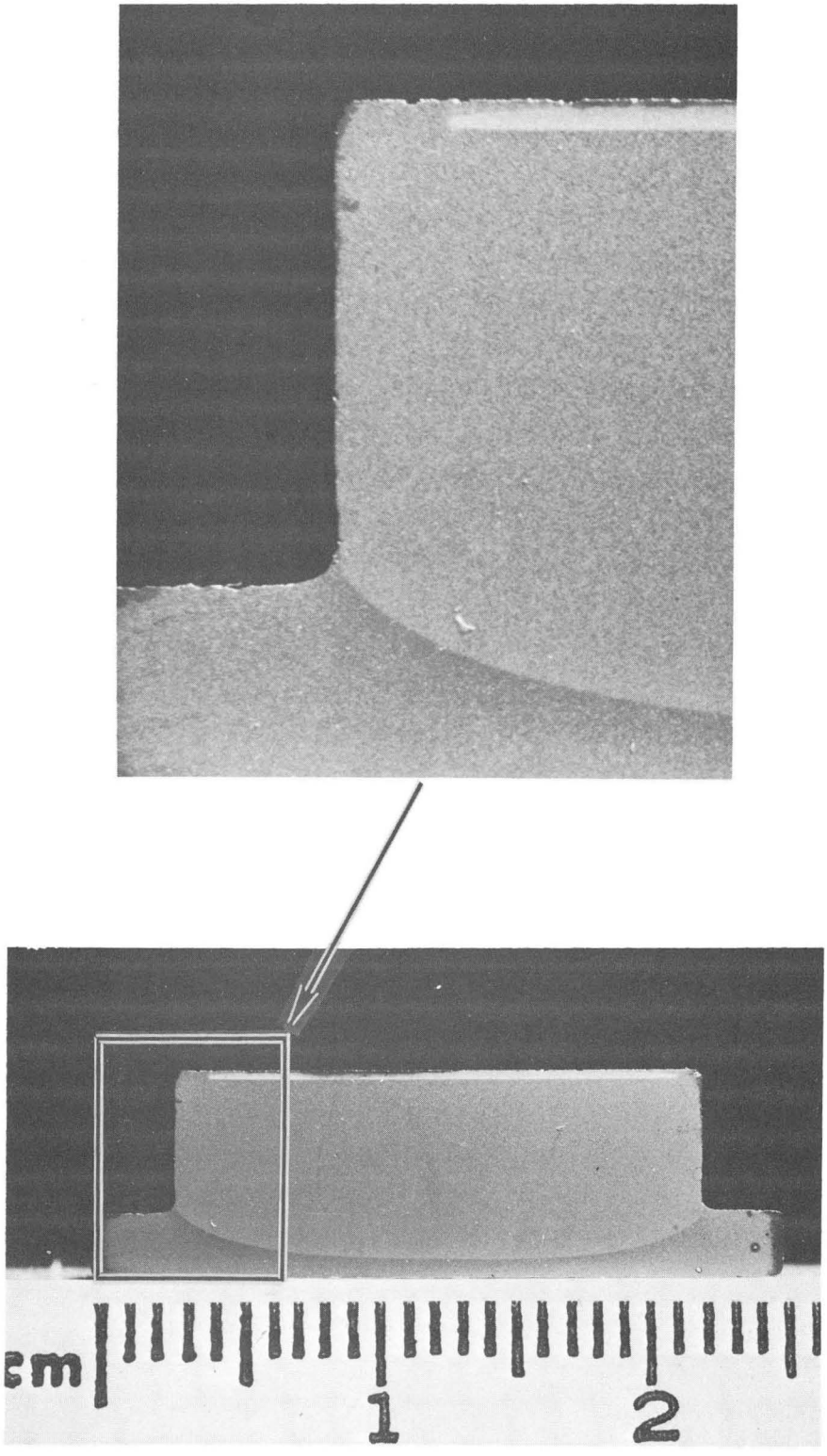
The field due to the drift voltage and the heavily p-type surface condition brings the drifting lithium ions to the surface in quantity. Their immediate oxidation upon reaching the surface irreversibly eliminates them from the drift process. Thus the effect of excessively p-type conditions is the massive loss of lithium from the N+ region at a rate which may preclude the successful drift of a deep device.

The surface loss of lithium distorts the shape of the advancing front of the intrinsic region. A near theoretical depth of drift is obtained at the center of the device and smaller depths of drift at the surface.

In addition to the above, observe, in Picture 1, that the N+ region is an island no longer meeting the surface.

Picture 2 shows the effects not only of excessively p-type drift conditions, but also the effect of non-uniform conditions.

When these results were first obtained, lithium precipitation, as seen in germanium detectors, appeared to be a likely source of the problem. However, heating to 400°C did not change the picture and eliminates precipitation as a cause of the lithium loss in these samples.



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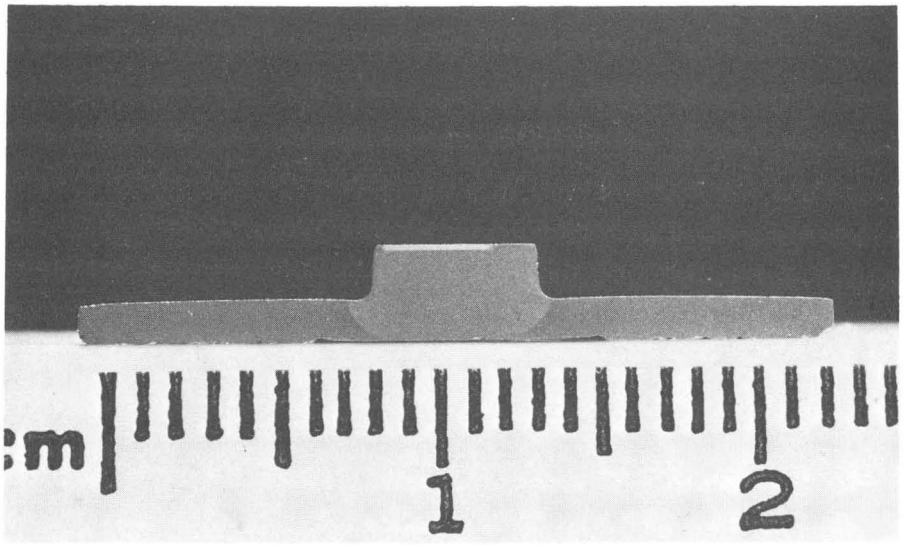
Picture 1



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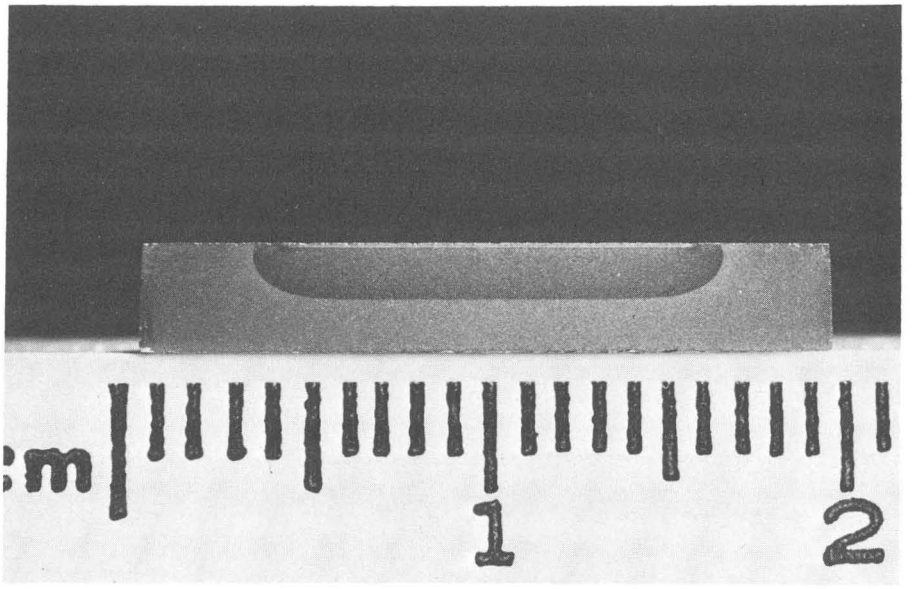
Picture 2

CASE 2 Planar Geometry - Excessively p-type Drift Conditions

Pictures 3 and 4

The detection of lithium loss from the N+ region is difficult in the planar geometry. In the top hat geometry, the method of fabrication is such that the N+ region terminates against a surface. Thus virtually any lithium loss from the edge of the N+ region is detectable. In the planar geometry, the diameter or length of the N+ region is not precisely controlled and lithium losses from the edge of this region are not at all obvious. However, what is evident is the distortion of the advancing front of the intrinsic region due to the loss of lithium from the surface.

Picture 4 also shows, in the intrinsic region, striations due to poor silicon quality.



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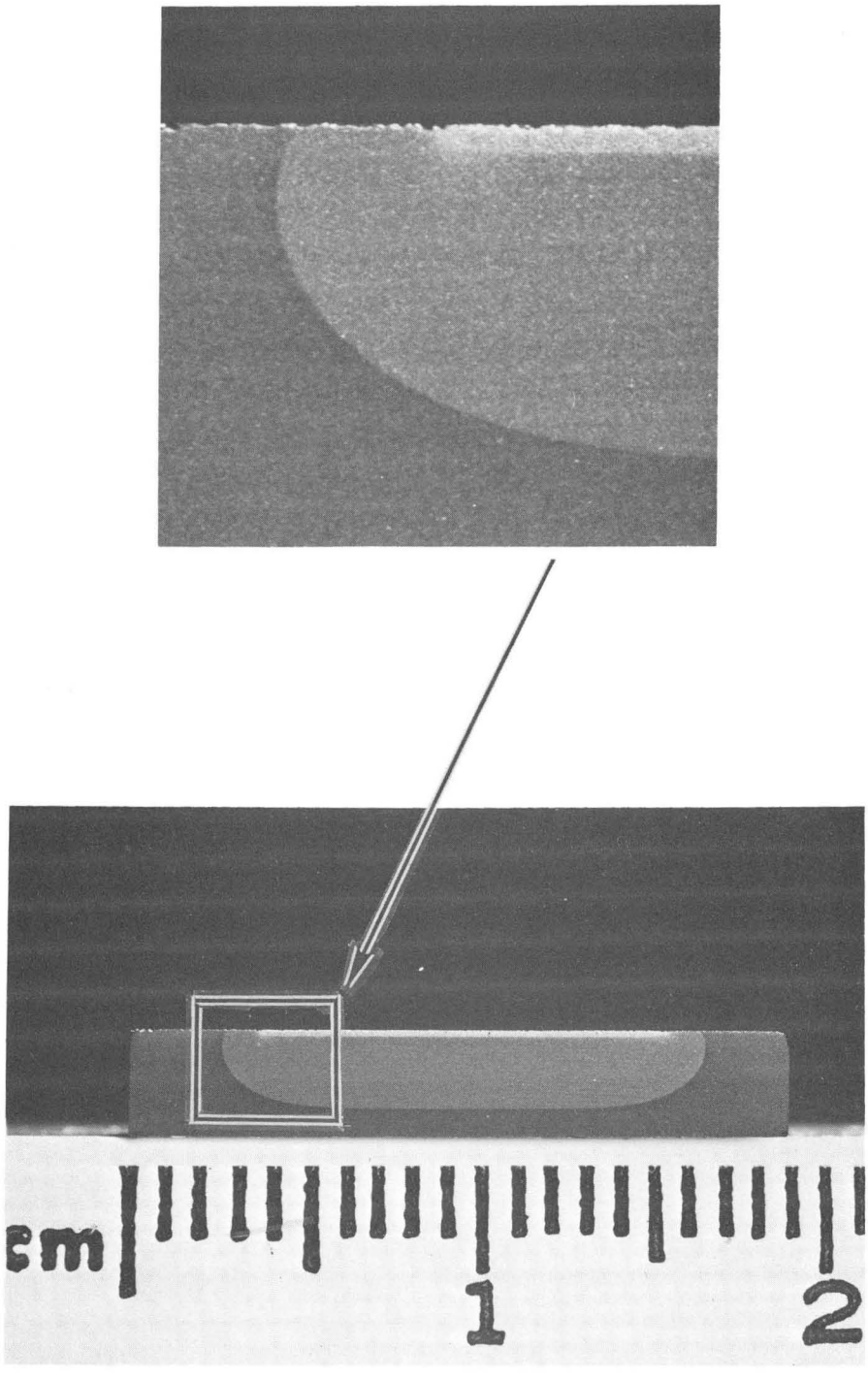
Picture 3



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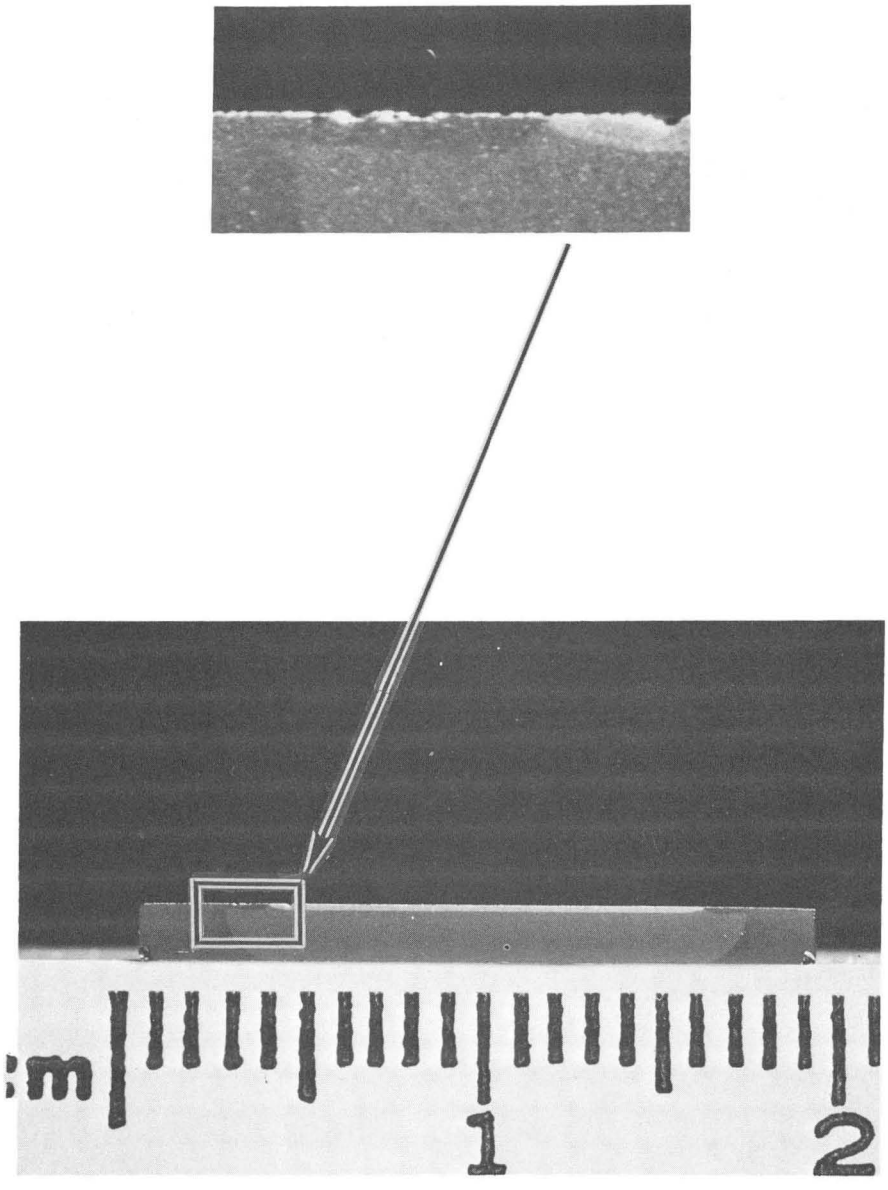
Picture 4

CASE 3 Planar Geometry - n-type Drift Conditions

Pictures 5 and 6

Under n-type conditions, a long surface channel extends from the N+ region. The field due to this surface channel is oriented such that any lithium in the region of this field is drifted out. No lithium ions can drift into this field region. Thus the surface peripheral to the N+ region remains uncompensated p-type material. The thickness of the uncompensated region depends, in part, on how heavily n-type the surface states are. The uncompensated region is thicker for heavily n-type conditions and thinner for lightly n-type conditions. Under heavily n-type conditions, the thickness of the p-type region is equal to the calculated depth of a depletion layer in the p-type material with the drift voltage applied to a n-type layer on it.

Picture 5 shows the results of uniform n-type surface conditions which contrast to the results of non-uniform surface conditions shown in Picture 6.



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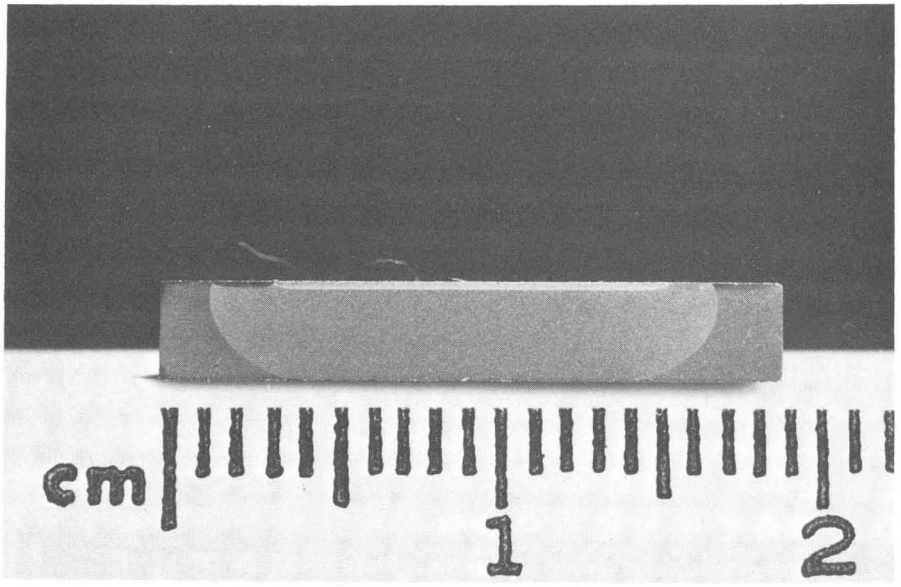
Picture 5



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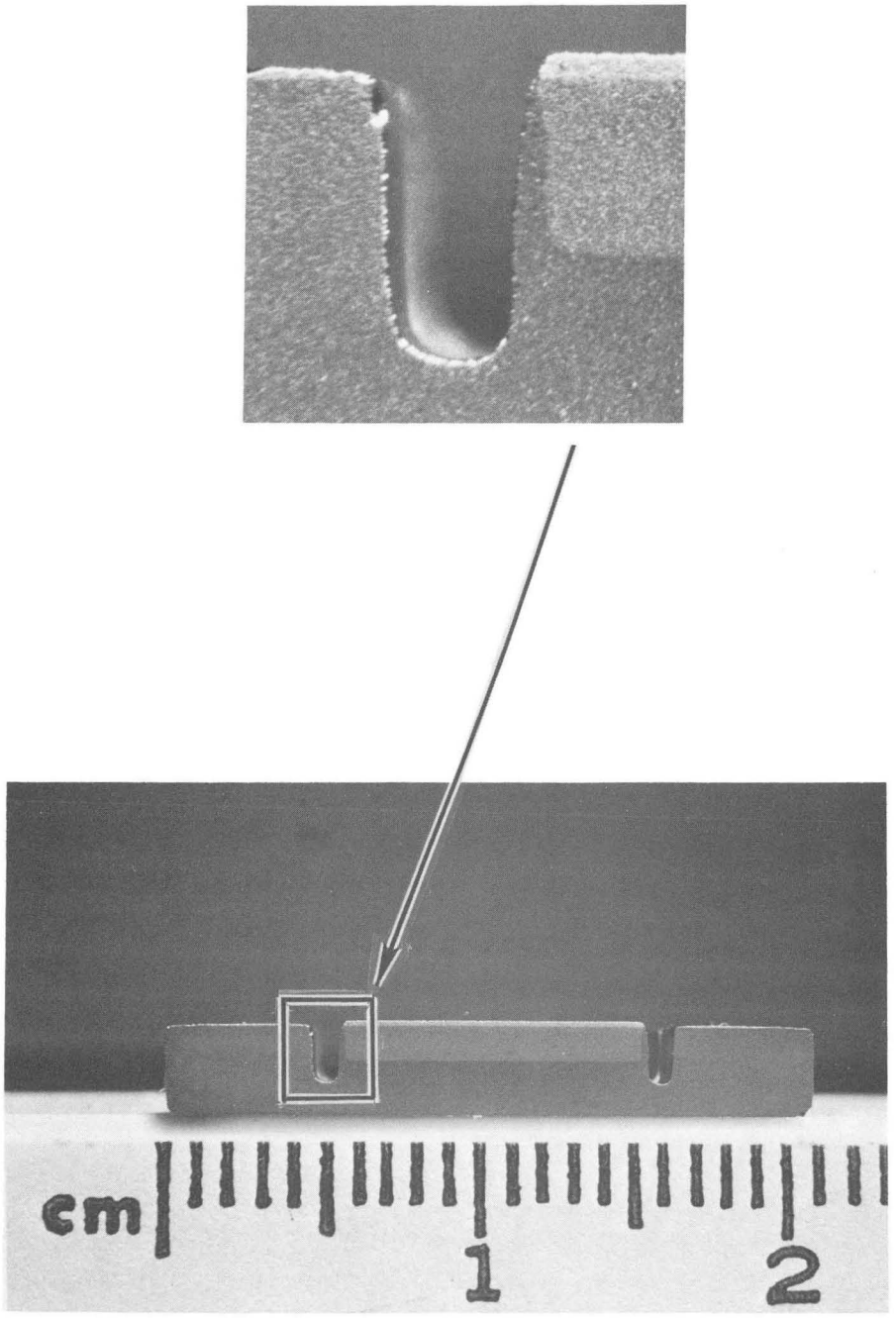
Picture 6

CASE 4 Saw Cut Geometry - n-type Drift Conditions

Picture 7

Note that the n-type conditions during drift caused the intrinsic surface to be short. The effect of this condition on the final electrical characteristics of such a device is that the final surface treatment is more critical (and difficult) than if the intrinsic surface were long.



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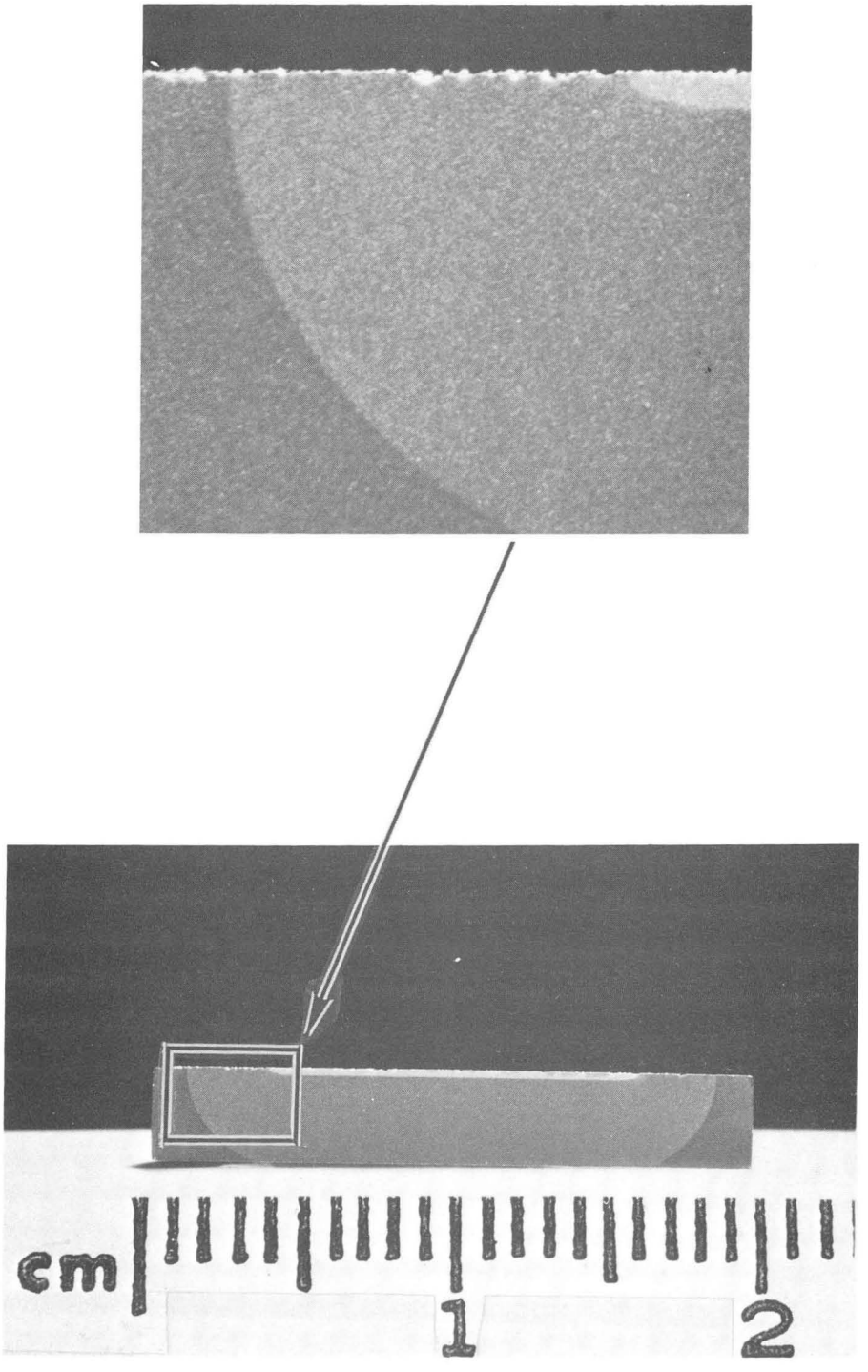
Picture 7

CASE 5 Planar Geometry - Lightly p-type Drift Conditions

Picture 8

Under lightly p-type conditions, the drift proceeds with a minimum of lithium loss at the surface. The drift depth along the surface is the maximum attainable, and the front of the intrinsic region meets the surface at nearly 90° tangentially.



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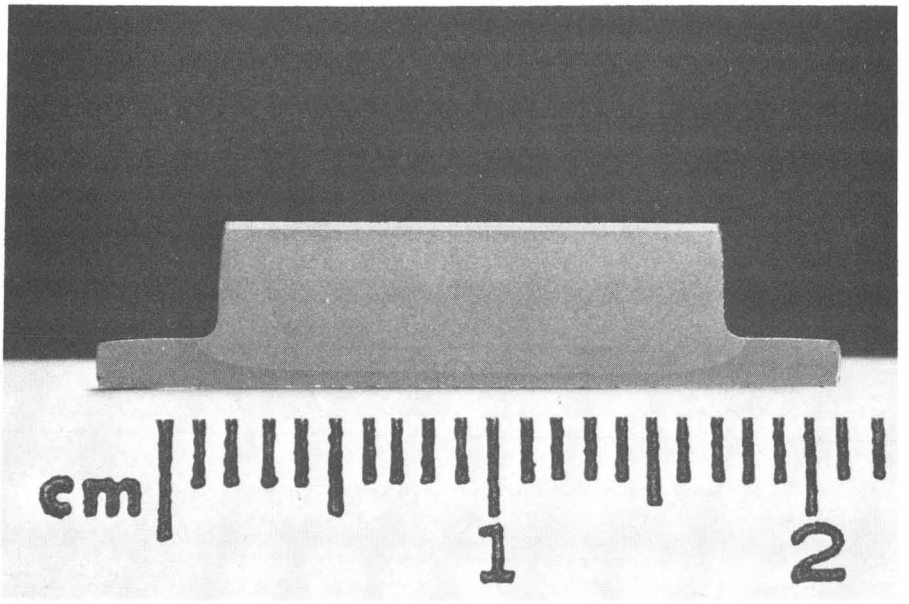
CASE 6 Top Hat Geometry - Lightly p-type Drift Conditions

Pictures 9 and 10

Observe in Pictures 9 and 10 that the intrinsic surface is long, that there is no detectable lithium loss from the N+ region, and that the front of the intrinsic region meets the surface at nearly 90° tangentially.

Picture 10 also shows, in the intrinsic region, striations due to poor silicon quality.



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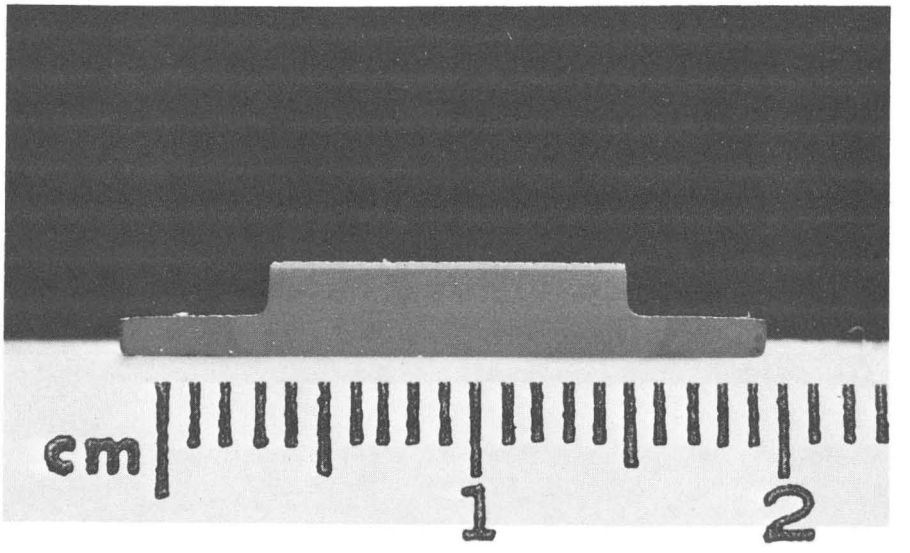
Picture 9



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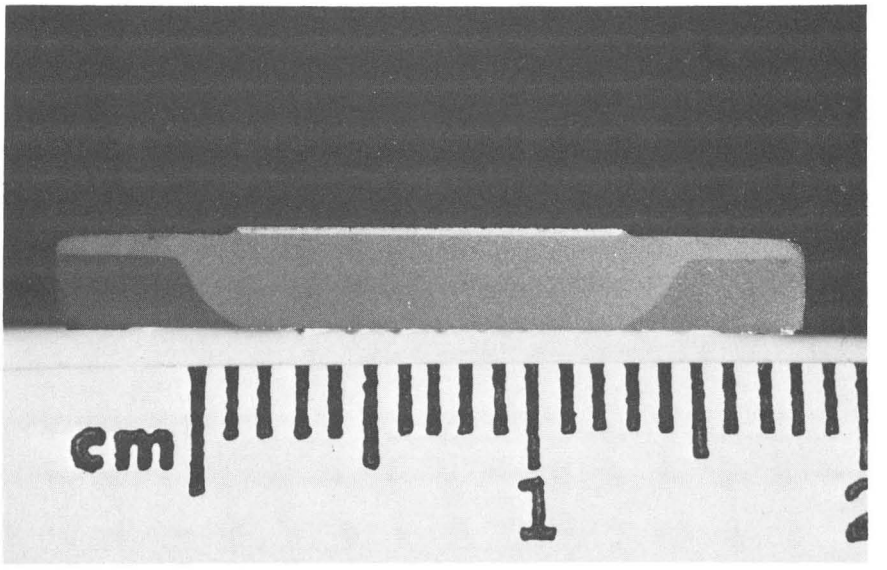
Picture 10

CASE 7 Etched Mesa "Double-Drift" Geometry - Lightly p-type Drift Conditions

Picture 11

This geometry has an extremely long intrinsic surface which must be properly prepared from an initial large area drift and which must remain intact through a subsequent drift.



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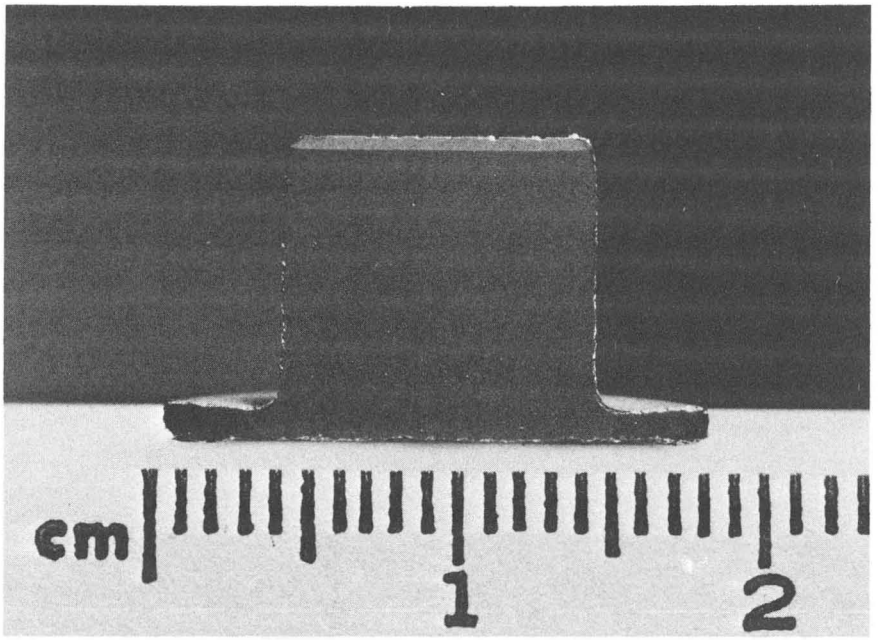
Picture 11

CASE 8 Top Hat Geometry 1cm Diameter by 1cm Deep
Lightly p-type Drift Conditions

Picture 12

The successful drift of a detector of this size requires that the drift system not only properly control the surface states, but also that it remove heat, in quantity, from the detector.

The pictured detector (Picture 12.) was fully completed as a useful device in a period of seven days. Note that the edge of the N+ region shows no sign of lithium loss, evidence of the very light p-type conditions of drift.



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Picture 12

PART IV

PRE-DRIFT SURFACE TREATMENT

Devices which have been, in all respects save surface state treatment, fully prepared for the drift operation, i.e., lithium diffused, geometry defined, etched, metallization applied, etc., are first given the following treatment:

1. Rinse with trichloroethylene.
2. Blow dry with dry nitrogen.
3. Soak in hydrofluoric acid for 30 seconds.
4. Rinse with methyl alcohol.
5. Blow dry with dry nitrogen.

The result of this treatment is that the surface states are uniformly, heavily n-type. For drift in the liquids discussed in Part VI, no further pre-drift treatment is necessary. For drift in the gas mixture $N_2 - I_2^v$, discussed in Part V, it is also the only pre-drift treatment used.

For drift in all other described gas mixtures, the following, and second, pre-drift treatment is required:

The HF treated devices are placed in helium bubbled, absolute ethanol held at 75° ± 0.1°C for exactly 60 minutes. At the end of this period they are immediately placed in absolute ethanol at room temperature for a period no longer than necessary to remove them serially and force dry them with dry nitrogen. The devices are then placed, as quickly as possible, in the drift apparatus in the proper gas mixture.

The result of this treatment is that the surface states are lightly p-type. A longer treatment will cause the surface states to become more heavily p-type. A shorter treatment will cause the surface states to remain n-type depending upon how short the treatment time becomes.

No other treatment affording such close control over the degree and type of the surface states has been discovered by this author.

Treatments such as H_2O (boiling soak) and H_2O_2 (soak) have been found to be so heavily p-type as to have, as yet, no useful application.

PART V

SURFACE STATE CONTROL
-DURING DRIFT- BY GAS MIXTURES

1. $N_2 - I_2^v$

An obvious first attempt at obtaining a lightly p-type gas mixture was the addition of a trace amount of a halogen to a commonly available gas. A drift system incorporating the gas mixture of nitrogen plus a trace amount of iodine vapor was used for production over a period of many months. This system was used to produce many fine drifted devices, but was finally changed to other gas mixtures for the following reasons:

1. The range of acceptable iodine vapor concentration was too narrow for proper control.
2. Corrosion of the metal parts of the drift apparatus was intolerable.
3. The nitrogen gas source used was not pure enough — the presence of variable amounts of oxygen changed the iodine vapor requirements and destroyed the stability of the system.

2. $He - CO_2$

With the discovery of a lightly p-type pre-drift surface treatment, the evaluation of helium as n-type, and carbon dioxide as p-type followed. This gas mixture affords almost unlimited control of the gas mixture type. At the start of drift, the optimum flow rate ratios (with lightly p-type pre-drift treated devices) are:

Planar Devices:	1:1
Top Hat and Saw Cut Devices:	$10He:1CO_2$.

Note that the control available under this gas system is such that the difference in electrical behavior between differing detector geometries can be taken into account.

The drifting of any device in this gas system lengthens the intrinsic surface. As this surface lengthens, the gas mixture must be shifted in the n-type direction to avoid lithium loss at the surface. For example, 3mm deep top hat or saw cut devices will require a flow rate ratio of about 30He:1CO_2 at the end of drift.

3. He - O_2

This gas mixture, as with the previous one, affords almost unlimited control of the gas mixture type: helium being n-type, and oxygen being p-type.

At the start of drift, the optimum flow rate ratios (with lightly p-type pre-drift treated devices) are:

Planar Devices:	1:1
Top Hat and Saw Cut Devices:	5He:1O_2

As before, the effect of the deep drifting of any device is to change the ambient requirements in the n-type direction. For example, 3mm deep planar devices will require a flow rate ratio of about 4He:1O_2 at the end of drift. After the first few hours of drift in the He - CO_2 or He - O_2 gas systems, the minimum of drift current is used as a gauge of the proper flow rate ratio. Representative 10mm diameter, 3mm deep top hat devices at 125°C and 500 volts will draw about 200 microamperes at the start of drift, and about 4 to 5 milliamperes at the end of drift.

PART VI

SURFACE STATE CONTROL

-DURING DRIFT- BY LIQUIDS

All liquids tested appear to take full control of the surface states the instant drift voltage is applied. Furthermore, the degree and type of any liquid tested has not been variable during drift. The choice must be a liquid which is lightly p-type under the drift conditions.

The following are the test results to date:

1.	FC-43 (3M)	Batch 1:	Excessively p-type
		Batch 2:	excessively n-type
2.	Benzene (Baker)		Excessively p-type
3.	Toluene (Baker)		Excessively p-type
4.	Xylene (Baker)		Excessively p-type
5.	cyclo-Octane (Aldrich)		Lightly p-type
6.	n-Nonane (Phillips 66)		Lightly p-type

The evaluation conditions included helium bubbling.

Of the above tested liquids, #6, n-nonane, used at its boiling point has yielded the best results. Reference to Part III, B, Case 8, will demonstrate the qualities of this liquid.

Xylene vapor (saturated) was also tested as a drift medium and was found to be excessively n-type.

The materials used to fabricate a liquid drift apparatus must be chosen with care. The presence of base metals (copper, lead, tin, iron, zinc, etc.,) must be avoided. Base metal oxides are sparingly soluble in these liquids and will plate as the oxide on the positive, high-voltage area of the drifting device. Furthermore, the liquid

should be freshly distilled to remove any traces of lint. Foreign materials in the liquid will be attracted to, and held by, the surface high-field region on the drifting device.

The apparatus used for liquid drifting is fabricated of the following materials:

1.	Container:	Pyrex.
2.	Metal Frame:	Solid Gold.
3.	Springs:	Heavily gold plated phosphor-bronze.
4.	Stand-offs:	Ceramic.
5.	Wiring:	90% gold, 10% Platinum wire.
6.	Insulation:	Teflon.
7.	Hardware:	Heavily gold plated brass.

FOOTNOTE AND REFERENCES

* This work was carried out as part of the research program of the Nuclear Chemistry Division of the Lawrence Radiation Laboratory, University of California, which is supported by U. S. Atomic Energy Commission Contract W-7405-eng-48.

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APPENDICES

Appendix 1. Guard Rings

The guard ring structure[4] can not, and is not intended to, improve the voltage and current characteristics of a detector AS A WHOLE. The guard ring structure does, however, afford a means of improving the resolution obtainable from any basic detector geometry. The guard ring structure may make two significant contributions to improve resolution:

1. Reduction of the leakage current contribution to the total noise.
2. Reduction of the capacity of the device.

The three variations of the guard ring structure, which may be applied to any basic detector geometry, are:

1. The N+ side, guard ring.
2. The gold side, guard ring.
3. The isolated, gold side, guard ring.

These combinations are shown in Table 1. These sixteen detector types do not exhaust the possible variations in either basic geometries, or their combinations with guard ring structures.

In virtually all lithium drifted silicon detector applications it is preferable to use a properly prepared basic geometry rather than any complex combination.

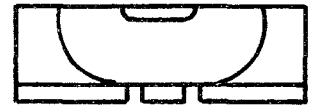
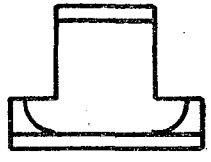
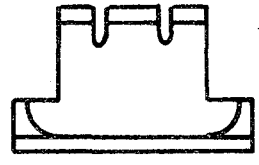
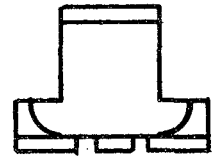
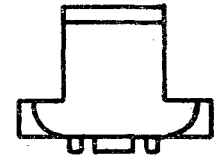
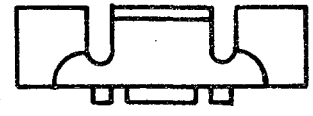
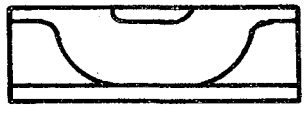
DETECTOR GEOMETRY, GUARD RING COMBINATIONS	BASIC GEOMETRY	THE N+ SIDE RING	THE GOLD SIDE RING	THE ISOLATED GOLD SIDE RING
PLANAR				
TOP HAT				
SAW CUT				
DOUBLE DRIFT				

TABLE 1

Appendix 2. Copper Stain Procedure

The copper stain solution has the following composition:

Copper Sulfate	20 gm.
Water	1000 ml.
Hydrofluoric Acid 48%	1 ml.

The silicon surface to be stained is carefully lapped with a fine lapping compound (Lapmaster 1900, WCA-9, etc.). This surface is rinsed clean and carefully dried to avoid water marks. The dry, clean, lapped sample is placed in a shallow dish and covered with copper stain solution. A bright light, such as a microscope lamp, is shone on the prepared surface of the sample for a period in the range of one-half to five minutes. The sample is then removed, rinsed with water, and force dried. If the viewing and incident light angles are low, the ease of examination may be improved.

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