

Ion Drift in an n - p Junction*

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(Received August 19, 1959)

If a reverse bias is applied to an n - p junction at a sufficiently elevated temperature to give either the donor or the acceptor ions appreciable mobility, the ions will drift in the electric field of the junction to produce an intrinsic semiconductor region between the n and p regions. Such ion drift offers a simple and straightforward method for investigating diffusion constants, as well as chemical interactions within the host lattice which affect this diffusion. Preliminary results indicate its feasibility for measuring the diffusion constant of Li in Si to as low as 10^{-18} cm²/sec and also for measuring the effect of Li-oxygen and Li-acceptor interactions in decreasing the diffusion rate. Intrinsic regions resulting from ion drift have been used to produce diodes with breakdown in excess of 4000 volts from low resistivity silicon. In addition, they can be used to extend the frequency range of devices by virtue of the decrease in junction capacitance associated with such an incorporated intrinsic region. Ion drift has also been used for the fabrication of analog transistors, an early unit having an input impedance of 6 megohms, a power gain of 17 db and a voltage gain of 4.

INTRODUCTION

USING the techniques to be described, it is possible to produce an intrinsic region between two heavily and oppositely doped semiconducting regions. This is of significance as a means for studying the drift-diffusion process and also as a new technique in device technology.

Since the ion drift process occurs on a microscale, measured distances being of the order of the width of the n - p junction, it is admirably suited to the measurement of small diffusion rates. The process is simple and straightforward and involves but few assumptions and parameters; one can hence have a high degree of confidence in the results. Because of the method's high sensitivity, (2.5×10^{-17} cm²/sec has been reliably measured with diffusion times of the order of hours; 10^{-18} cm²/sec appears quite reasonable) it can be used to measure diffusion rates at relatively low temperatures, where chemical interactions are expected to affect the diffusion rate,¹⁻³ and it leads directly to the value of the binding energy in such interactions. Because it sensitively measures the diffusion rate at very low concentrations (10^{13} atoms per cc or lower for Li in Si) it can measure the effect of chemical constituents which are present in comparably low concentrations.

In device technology, the advantages of p - i - n diode structures and related transistor structures as a means of increasing the breakdown voltage and high-frequency limit have long been known.^{4,5} The ion drift technique offers another method for achieving such structures. It

eliminates the need for using material of intrinsic resistivity and hence may prove useful with semiconductors of low purity. Also, it offers a new degree of freedom in controlling device geometry, particularly on the microscale; and it may therefore prove applicable in certain special areas of device technology. Its usefulness in achieving complex geometries is illustrated by its adaptability to making an analog transistor structure—so called because it is exactly analogous to the structure of the vacuum tube, inclusive of control grid, with a drift region composed of intrinsic semiconductor replacing the vacuum of its counterpart. The concept of such a structure probably antedates the transistor. Possible forms have been described in detail,⁶ and a close variant has been produced,⁷ but only with the ion drift technique has it now become possible to achieve the exact counterpart of the vacuum tube.

The method for achieving an intrinsic region by use of ion drift relies on the drift of donor and/or acceptor ions in the field of a reverse-biased n - p junction. It will be demonstrated that the ions drift in such a way as to almost perfectly compensate each other. The temperature at which this occurs must, of course, be sufficiently high to make either the donor ions or the acceptor ions mobile, but not so high that the semiconductor becomes intrinsic and the n - p junction disappears.

PRINCIPLES OF THE ION DRIFT PROCESS

We shall consider the drift of Li⁺ ions, which are donors, in p -type Si, the latter being produced, for example, by doping with boron during the crystal growth. The acceptor is initially present uniformly throughout the Si to a level of N_A acceptors per cc. Lithium is then diffused into the silicon from a surface source of N_0 donors per cc, where $N_0 \gg N_A$, until an n - p junction is produced internally at the position $x=c$, as

* The research reported in this paper has been partly sponsored by the Electronics Research Directorate of the Air Force Cambridge Research Center, Air Research and Development Command, under contract AF 19(604)-5551. It has been presented, in part, at the May, 1959 meeting of the Electrochemical Society.

¹ Reiss, Fuller, and Morin, *Bell System Tech. J.* **35**, 535 (1956).

² J. P. Maita, *J. Phys. Chem. Solids* **4**, 68 (1958).

³ E. M. Pell, *Proceedings of the Brussels Conference on Solid State Physics, 1958* (to be published).

⁴ A. Uhler, Jr., *Proc. Inst. Radio Engrs.* **46**, 1099 (1958), and references therein.

⁵ J. M. Early, *Bell System Tech. J.* **33**, 517 (1954).

⁶ W. Shockley, *Proc. Inst. Radio Engrs.* **40**, 1289 (1952).

⁷ Stutz, Pucel, and Lanza, *Proc. Inst. Radio Engrs.* **45**, 1475 (1957).

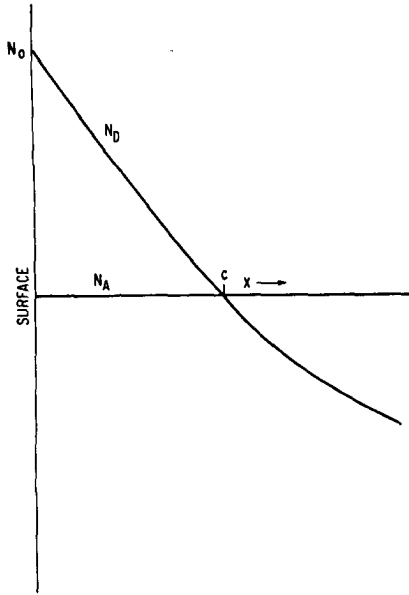


FIG. 1. Impurity distribution after preliminary lithium diffusion.

in Fig. 1. For diffusion temperatures sufficiently high that drift in the built-in field of the junction is negligible, the initial donor concentration as a function of the distance, x , from the surface is described by⁸

$$N_D = N_0 \operatorname{erfc}[x/2(D_0 t_0)^{1/2}] \quad (1)$$

where D_0 is the diffusion constant at the temperature of this initial diffusion and t_0 is the duration of the diffusion period. We shall consider only the region of large x in the neighborhood of $x=c$, with $c \gg (D_0 t_0)^{1/2}$. In this region Eq. (1) can be approximated by the first term of a series expansion, giving

$$N_D \simeq (2N_0(D_0 t_0)^{1/2}/x\sqrt{\pi}) \exp(-x^2/4D_0 t_0). \quad (2)$$

At $x=c$, this equation becomes equal to N_A , permitting an evaluation of $N_0(D_0 t_0)^{1/2}$. Substituting this in Eq. (2),

$$N_D \simeq (N_A c/x) \exp[-(x^2 - c^2)/4D_0 t_0]. \quad (3)$$

We note, for future use, that for values of x in the neighborhood of c , Eq. (1) can be expanded by Taylor's formula to give

$$N_D \simeq N_A [1 - (x-c)/L + (x-c)^2/2L + \dots] \quad (4)$$

where $L \equiv 2D_0 t_0/c$. The slope at $x=c$ is $(-N_A/L)$.

If a reverse bias is now applied to this n - p junction, an electrostatic field (E) will be present in the space charge region extending a short distance in both directions from $x=c$. This field will exert a force tending to move the positively charged Li^+ ions from the Li-rich side of the junction to the Li-deficient side. Such Li-ion motion will occur in a reasonable time, provided the

temperature is sufficiently high to give the Li^+ ions appreciable mobility (μ). The number of Li^+ ions per cm^2 moved across the junction in time t will be $E\mu N_A t$, the N_A arising from the fact that the field exists only in the region where $N_D \simeq N_A$. This relation depends on the assumption that the field is large enough so that $E\mu N_D \gg D\nabla N_D$, i.e., so that the drift exceeds any diffusion which can occur. In this case the Li^+ concentration at $x < c$ will decrease and the Li^+ concentration at $x > c$ will increase. The Li^+ concentration cannot, however, fall below N_A at $x < c$ because the excess acceptors in such a region would change the space charge so as to increase the field on the excess Li^+ side and decrease it on the opposite side, thus increasing the Li^+ flow into the deficit region until it disappeared. For similar reasons, the Li^+ concentration cannot rise above N_A at $x > c$. The value of N_D will, therefore, tend toward N_A at $x < c$ and rise toward N_A at $x > c$, thereby producing an intrinsic region and extending the region in which the driving field, E , is present. This is illustrated in Fig. 2, which shows the impurity concentrations after such a drift period. In this figure, the gradient of N_D at the steep region near $x=a$ will be given roughly by $D\nabla N_D = E\mu N_D$ since it is this concentration gradient in the zero-field region that supplies ions by diffusion to the drift region. Because of the large E the concentration gradient of N_D in this diffusion region will hence generally be steep relative to the initial gradient. The steep region near $x=b$ can be even steeper than the one near $x=a$ because of ion pairing.¹ We shall approximate both steep regions by vertical lines. The amount of Li drifted in time t is then represented by the shaded area, or

$$\int_0^t E\mu N_A dt = \left(\int_a^c N_D dx \right) - (c-a)N_A \\ = (b-c)N_A - \int_c^b N_D dx. \quad (5)$$

Using Eq. (1) for N_D and integrating by parts there is obtained

$$\int E\mu N_A dt = cN_0 \operatorname{erfc}[c/2(D_0 t_0)^{1/2}] \\ - aN_0 \operatorname{erfc}[a/2(D_0 t_0)^{1/2}] + [2N_0(D_0 t_0)^{1/2}] \\ \sqrt{\pi} [\exp(-a^2/4D_0 t_0) - \exp(-c^2/4D_0 t_0)] \\ - (c-a)N_A \quad (6)$$

with a similar expression involving b and c . To find the behavior near $t=0$, for $W \ll L$, the erfc and the exponential can be expanded about c , giving

$$\int E\mu dt \simeq (c-a)^2/2L + (c-a)^3/6L^2 \\ \simeq (b-c)^2/2L - (b-c)^3/6L^2 \quad (7)$$

⁸ Carslaw and Jaeger, *Conduction of Heat in Solids*, (Oxford University Press, London, 1959), second edition, p. 60. There may be some error caused by built-in fields if the concentration near the surface is high enough to make a part of this region extrinsic during the diffusion;¹⁷ this effect will be neglected here.

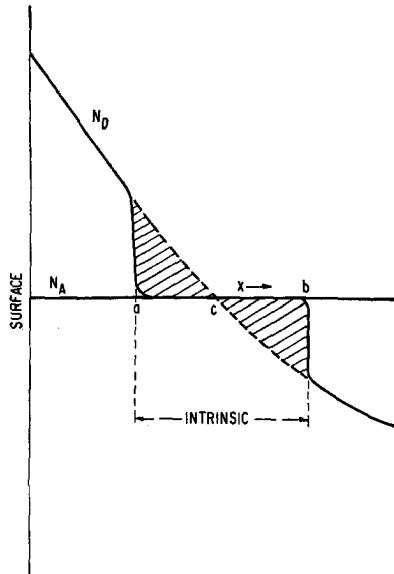


FIG. 2. Impurity distribution after ion drift.

from which, with further manipulation, there is obtained for $W = (b-a) \ll L$:

$$\int E\mu dt \simeq (W^2/8L), \quad (8)$$

with an error less than $W^2/27L^2$, as obtained by calculating the next term. Thus, for drift in a constant field, the square of the junction width will be proportional to the drift time; or for a constant applied voltage (approximately equal to the field times the junction width), the cube of the junction width will be proportional to the drift time.

For t very long or for $W \gg L$, on the other hand, it is not convenient to expand the erfc and exponential in Eq. (6) about c because too many terms would be required for a good approximation. It is in this case more appropriate to use the asymptotic series for the erfc of large argument, giving

$$\begin{aligned} \int E\mu dt &\simeq L\left\{ \frac{c^2}{a^2} \exp\left[\frac{c^2-a^2}{4D_0t_0}\right] - 1 \right\} + a - c \\ &\simeq b - c - L\left\{ 1 - \frac{c^2}{b^2} \exp\left[\frac{c^2-b^2}{4D_0t_0}\right] \right\}. \end{aligned} \quad (9)$$

This yields, for $(b-c) \gg (c-a) \gg L$, and hence for $W \simeq (b-c)$,

$$\int E\mu dt \simeq W. \quad (10)$$

The junction width will now be proportional to the drift time for constant field, or the square of the junction width will be proportional to the drift time for constant voltage. For t very long, the source becomes very "stiff" because the intrinsic region has moved back to a steep region of N_D at $x < c$, and growth occurs

primarily at $x > c$, where each increment in x must be filled with donors to the constant concentration N_A .

These preliminary remarks have been intended to describe the physics of the drift process in easily understood terms, and mathematical complications arising from the initial space charge width have been neglected. In order to confirm the model experimentally, it is necessary to include these complexities, and also to include accurately the effect of varying E for constant applied voltage. This has been done in the Appendix, to which reference will be made in discussing the experimental results.

EXPERIMENTAL TECHNIQUES

1. Normal Technique

The ion drift process is straightforward and involves the measurement of but few parameters. In the simplest case, namely the measurement of ion mobility after appreciable initial drift, one needs to measure only the junction area and the variation of capacitance with time with constant applied voltage. Normal precautions are necessary in making contact to the sample to ensure that the junction capacitance, and not some capacitance associated with the contact, is measured. This generally requires the use of some form of alloyed or diffused contact to the p -type region. We have successfully used alloyed Al, alloyed Au, and diffused B. Since the Li-diffused n -type region has very low resistivity at the surface, a simple pressure contact to this region generally suffices. In Si of less than 10 ohm-cm resistivity, measurements can be made in room air with little danger that inversion layers will affect the capacitance measurement. It is advantageous to use a high-sensitivity bridge with provision for measuring direct capacitance exclusive of stray capacitance via ground; it is also advantageous for the measuring instrument to afford dc continuity so that bias voltage can easily be supplied in series with bridge and sample. Because of the loss associated with the reverse leakage current, the use of a high-frequency bridge (e.g., 100 kc) is recommended; and because of the voltage dependence of the junction capacitance, the ac measuring voltage of the bridge should be small.⁹

2. Inversion Layers

In higher resistivity Si, inversion layers become troublesome because they add to the junction capacitance and often vary in an unpredictable fashion. Their presence has been confirmed and their behavior studied in high resistivity samples by observing the change in contact potential with weak illumination, using a chopped-light technique. Since the Li^+ gradient is quite steep and hence inhibits inversion a very short distance from the junction on the Li^+ side, this trouble generally

⁹ In the present experiments, a Boonton 74-C capacitance bridge was used.

is most serious on the *p*-type side. In 100 ohm-cm Si, inversion can be controlled satisfactorily by the use of a dip in dilute (about 0.1%) sodium dichromate solution after etching the junction, with subsequent measurements made in dry oxygen.¹⁰ In 1000 ohm-cm Si, such treatment has not sufficed, and to prevent surface inversion effects it has been necessary to make the surface strongly *p*-type by a two hour diffusion of B at 1150°C (after a one-minute treatment in BCl₃ at 1150°C)¹¹ followed by a subsequent removal of the amorphous boron by an etching process.¹² Subsequent to this surface treatment, one face is ground off and the Li alloying and diffusion performed on this face in the manner to be described. The thin shell (of the order of 1 μ thick) of high-conductivity B-doped Si cannot in any case contribute appreciably to the capacitance, but its effect is additionally minimized in that it, too, becomes intrinsic in the drift process. This boron-diffused layer has a further usefulness in affording a low resistance contact to the sample. This contact is made by electroplating the *p*-type skin with gold prior to the Li diffusion. Electroless Ni plating has also been used, but it leads to heat-treatment effects from diffusion of Ni into the Si during the Li diffusion, these effects showing up as resistivity changes and hence junction capacity changes during the first few hours at room temperature after the Li diffusion.

3. Heat Treatment Effects

In 1000 ohm-cm Si, even though produced by the floating zone process, impurities can be introduced during the predrift treatments which lead to changes in sample resistivity. Although such heat treatment effects have been noticed, they are not serious in practice, being present only in very high resistivity Si and only for the first few hours at room temperature. They do not affect the results at long *t*, and for higher temperature ion drift their effects can be eliminated by allowing the sample to stand for a few hours at room temperature, without applied drift voltage, previous to the drift. The high-temperature boron diffusion does not seem to be responsible for such heat treatment. The Li diffusion step seems rather to be the cause in that it permits the simultaneous diffusion of an impurity (probably copper) into the sample, which causes resistivity changes having time constants of the order of hours at room temperature—similar in some respects to the effect of Ni, but generally going in the opposite direction. We believe the troublesome impurity to be copper because it has an appropriate diffusion rate, and its deliberate introduction produced a similar, but enhanced, effect. When it is necessary to observe the initial drift, it has been found that this effect can be

greatly minimized, though never entirely removed in 1000 ohm-cm Si, by very lightly gold plating the entire sample, producing little more than a haze, subsequent to grinding the sample face for Li diffusion. The sample is then heated overnight at 320°C, enabling the Au to act as a chemical getter in removing the Cu. In the Li diffusion, the Li is added on top of this gold film so that the Au will be present during the Li diffusion.

4. Li Diffusion

Li is normally added by painting a Li-in-oil suspension¹³ on one face of the sample, which is typically of dimensions 1 cm×0.3 cm×0.3 cm. This is then dried at about 200°C in helium. For drift measurements at long *t*, where initial phenomena are of no concern, the Li diffusion can then be performed by simply raising the temperature to 450°C for 1½ minutes, without worrying about what may happen during the ensuing quench. Where initial phenomena are of concern, it is necessary to ensure a fast quench so that these phenomena will not occur during the quench itself. It is also desirable to know the diffusion time and temperature accurately to give an additional means, other than initial capacitance, for calculating the initial Li⁺ distribution. We have used a graphite double-strip heater, forming an approximate blackbody enclosure, with the sample resting flat upon the lower strip and within a few millimeters of the upper strip. To ensure accurate measurement of the diffusion time, an initially-peaked current wave form has been used to heat the graphite

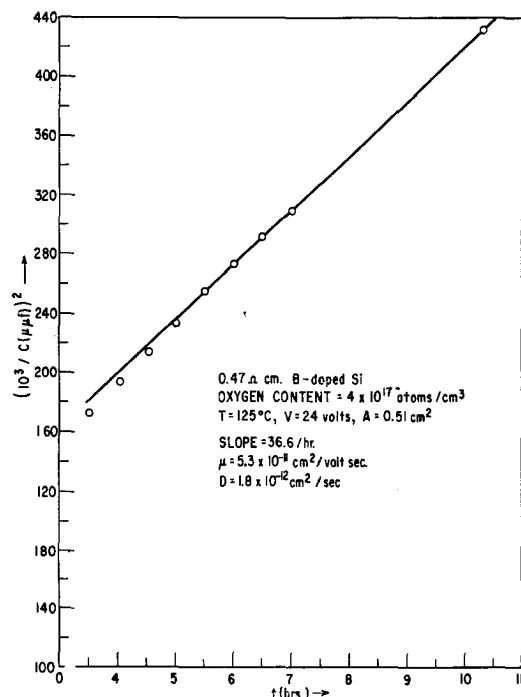


FIG. 3. $(1/C)^2$ vs time at long *t*.

¹³ 30% Li, 70% mineral oil, 1.7% oleic acid; available from the Lithium Corporation of America.

¹⁰ H. Nelson and A. R. Moore, RCA Rev. 17, 5 (1956).

¹¹ *Transistor Technology III* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1958).

¹² M. Waldner (private communication).

strips to 450°C in about one second. Temperature has been monitored by a calibrated lead sulfide cell and chopper and manually maintained at 450°C during the diffusion period. A fast quench has been obtained by blowing the sample with a high-velocity nitrogen jet into a room-temperature ethylene-glycol bath about 6 in. distant, taking care to ensure a straight line, non-turbulent path. After the quench, the sample is etched quickly in dilute white etch and mounted in the measuring jig, generally under a flowing dry oxygen ambient. If the reverse current is too high, the unit is re-etched until the loss component falls within the tolerance of the bridge.

VERIFICATION OF THE ION DRIFT MODEL

Since the model as developed in the first section and in the Appendix relies on various approximations to predict the behavior over a range of physical parameters, one would like to verify each of these approximations experimentally. In this section, those con-

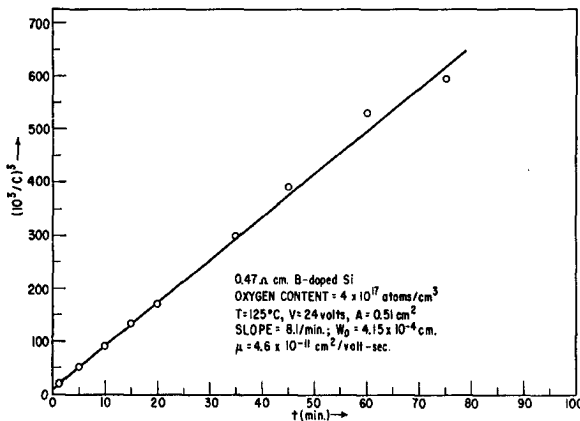


FIG. 4. $(1/C)^3$ vs time at short t .

clusions of the model which can be subjected to experimental test will be enumerated and compared with experiment.

1. For constant applied voltage, the square of the junction width should vary linearly with time at long t . Such behavior has been observed for every sample tested. An example is exhibited in Fig. 3. The square of the reciprocal capacitance, and hence the square of the width, is seen to approach a straight line asymptotically at long t .

2. For constant applied voltage, the cube of the junction width should vary linearly with time at short t , when $W_0 \ll L$. Such behavior is illustrated in Fig. 4, for the same sample of Fig. 3 discussed in the preceding paragraph. Another example is illustrated in Fig. 9.

3. The slope at $t=0$ should be uniquely related to the slope at long t , in accordance with Eq. (A37) of the Appendix. This can be verified by comparing the mobility calculated from Fig. 3, using Eq. (A8) of the Appendix, with the mobility calculated from Fig. 4,

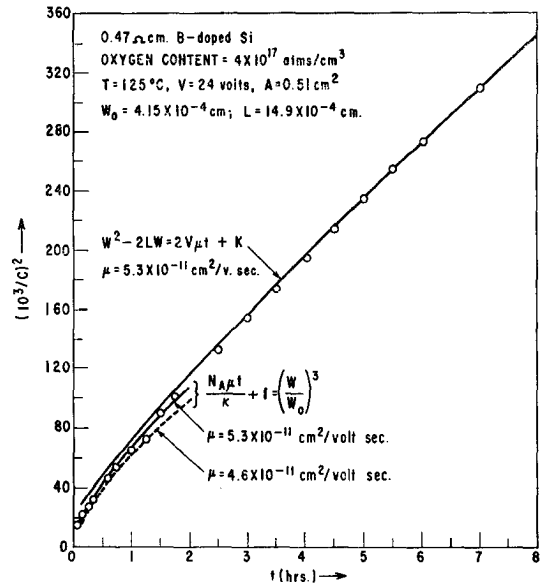


FIG. 5. $(1/C)^2$ vs time, calculated and experimental.

using Eq. (A21) of the Appendix. The two mobilities are 5.3×10^{-11} cm²/volt sec and 4.6×10^{-11} cm²/volt sec, respectively. This constitutes good agreement. The discrepancy could arise either from an error in the determination of the area, or from an error in the value of N_A as determined from the resistivity. The latter seems more likely in view of the spread in the values of N vs ρ reported in the literature. We used a value of 4.3×10^{16} /cm³ for N_A in this 0.47 ohm-cm Si, using the data of Prince.¹⁴ A value of 3.73×10^{16} /cm³ for N_A would have resulted in perfect agreement in the μ obtained from Fig. 3 with that obtained from Fig. 4. Other values of N_A obtained from the literature¹⁵ range from 3.5×10^{16} /cm³ to 8×10^{16} /cm³ for this resistivity.

The results can be displayed in a different form by using the calculated μ to plot two theoretical curves for short t and long t , using Eqs. (A10) and (A22) of the Appendix, and comparing these with the experimental data. This has been done in Fig. 5. Again the agreement is excellent.

4. Also in accordance with Eq. (A37) of the Appendix, the initial slope should become more nearly equal to the final slope, on a plot of W^2 vs time, as the resistivity of the starting material increases. This is illustrated by Fig. 6, which shows that in high resistivity silicon (1800 ohm-cm) the initial slope becomes indistinguishable from the final slope. It is possible, of course, that a different initial slope exists for too short a time to be seen, i.e., that the time constant for the

¹⁴ M. B. Prince, Phys. Rev. **93**, 1204 (1954).

¹⁵ G. Backenstoss, Phys. Rev. **108**, 1416 (1957), and references cited therein.

¹⁶ F. J. Morin and J. P. Maita, Phys. Rev. **96**, 28 (1954), with N_A calculated from the conductivity mobility given by their Figs. 11 and 14.

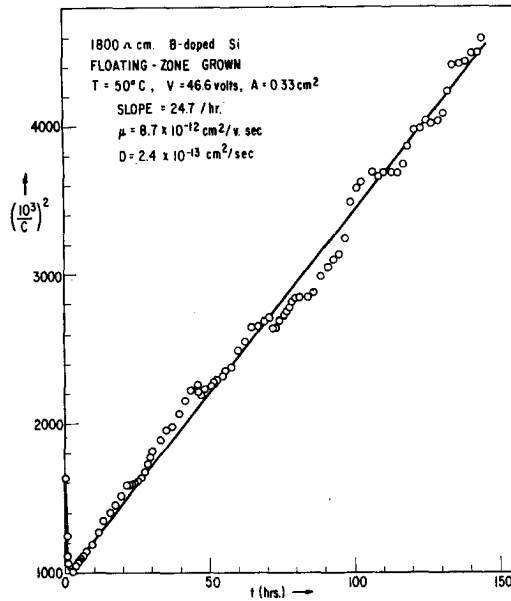


FIG. 6. $(1/C)^2$ vs time in 1800 ohm-cm Si.

disappearance of an initial region of different slope decreases as the resistivity increases. The present treatment does not answer such a question. The conservative interpretation of Fig. 6 is that it does not disagree with Eq. (A37) of the Appendix. The initial drop in Fig. 6 is felt to be caused by a heat treatment effect, as discussed in the section on experimental techniques. The fluctuations in the data are typical of high resistivity samples, and their cause has not been determined. The fact that the measured capacitances are here very small, as low as $15 \mu\text{mf}$, will introduce some statistical fluctuation. In addition, the presence of fluctuations in resistivity could lead to such data fluctuations.

5. If ion drift produces the impurity distribution indicated in Fig. 2, then the space charge will be largely localized near a and b , and the capacitance should hence become essentially independent of voltage after ion drift. A typical C - V characteristic after ion drift is reproduced in Fig. 7. The significant feature is that the capacitance becomes independent of voltage only above the voltage which was applied during the ion drift and exhibits a roughly $V^{-3/2}$ dependence below this voltage. This has been checked for other drift voltages. The $V^{-3/2}$ region indicates that there is some uncompensated charge present in the region which we have called intrinsic. It is therefore important to know whether the quantity of uncompensated charge is significant—in particular, whether the field can be treated as constant throughout the drifted region, as we have done, or whether this region should be treated as a gradient junction with the field dropping to zero at the edges. The precision of the CV characteristic is insufficient to answer this question. But an argument can be made which indicates that the constant field approximation is the best one to use, as follows: The ion current at the

position of E_{max} is given by $E_{\text{max}}\mu N_A$. If the field drops to a small value at the edge of the junction, i.e., if the junction is gradient-type, this quantity is equal to $(dN/dx)W^2\mu N_A/8\kappa$, where E_{max} has been determined by solving Poisson's equation for a gradient-type junction. W is the junction width and κ the dielectric constant. If the field drops to a small value at the edge of the junction, this same current would at that point need to be carried by diffusion. But the diffusion current is just $D(dN/dx)$, where dN/dx at the junction edge is comparable to dN/dx at the position of E_{max} in a gradient junction. The ratio of this value for the diffusion current to the preceding value for the field current is thus $8\kappa kT/W^2qN_A = (1.2 \times 10^6)/W^2N_A$, where k is Boltzmann's constant and q is the electronic charge. In our samples of smallest W ($\sim 10^{-3}$ cm) and smallest N_A ($\sim 10^{18}$ cm $^{-3}$) this ratio is only about 10%, indicating that diffusion is incapable of supporting the ion current near the junction edge and that the electric field must hence be appreciable near the junction edge—in fact, nearly as large as at the position of E_{max} .

6. If the quench is sufficiently fast, the initial capacitance should give the same value for the initial junction width, W_0 , as is obtained from calculating this quantity from a knowledge of the diffusion time and temperature. The junction width is related to the capacitance by $W_0 = 1.06 A/C_0$, where A is the area in cm 2 and C_0 is the initial capacitance in micro-microfarads. W_0 is also related, through a solution of Poisson's equation, to the gradient at the junction by $W_0 = (12\kappa VL/qN_A)^{1/2}$ where $L = N_A/(dN/dx)$ and V is the applied voltage. L is given by $2D_0t_0/c$, where D_0 and t_0 are the diffusion constant and the diffusion time, respectively, and c is the distance from the surface to the junction [see Eq. (4)], which can be found from the complementary error function solution to the diffusion equation [see Eq. (1)]. In a typical junction so tested (the same junction described by Figs. 3–5), W_0 determined from the initial capacitance, making a slight correction for ion drift occurring at room temperature prior to the measurement, was 4.94×10^{-4} cm. Calculated from D_0 and t_0 , the corresponding value was 4.15×10^{-4} cm. The former value is subject to two errors: (a) if the quench is faulty, some drift may occur

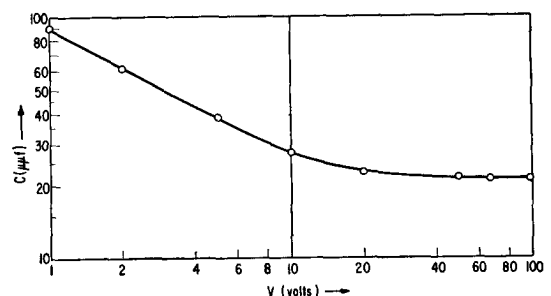


FIG. 7. Capacitance-voltage characteristic after ion drift at 24 volts.

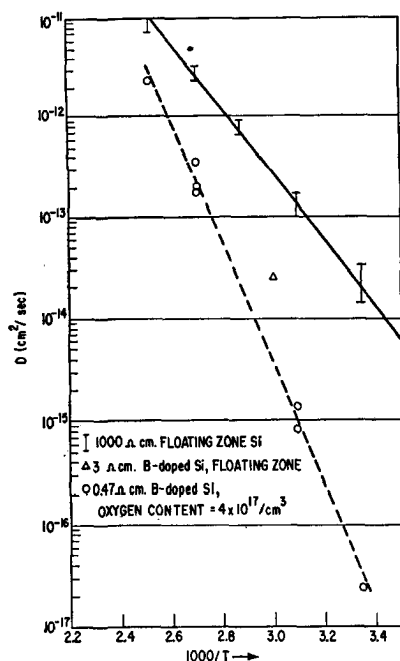


FIG. 8. Diffusion rate of Li in Si; preliminary results.

in the built-in field during the quench, causing the measured $1/C$, and hence W_0 , to be too large; and (b) if the alloying is at all spotty, the value used for the area will be too large, leading also to a W_0 which is too large. The latter value for W_0 is hence felt to be the more accurate; though it, too, is subject to a small error because of the effect of the built-in field in the extrinsic region during the diffusion, arising from the disparity in diffusion rates of electrons and ions.¹⁷ Note that W_0 cannot generally be found by extrapolating drift data to zero time, especially in high temperature runs, because the zero of time is not accurately known, some ion drift inevitably occurring while the sample is brought to temperature. With a slower quench, W_0 from the initial capacitance was generally significantly too large, suggesting that some ion drift took place during the quench itself, probably from the built-in field of the junction. For example, one ohm-cm p -type Si becomes intrinsic around 350°C ; at this temperature the diffusion constant of Li is of the order of 10^{-8} cm²/sec and μ of the order of 10^{-7} cm²/volt sec, leading to drift rates of the order of 10^{-4} cm/sec for a junction 10^{-4} cm wide with 0.1 volt for the "built-in" junction voltage.

7. If there are no systematic errors present in the analysis of the model, and if precautions are taken to use Si of sufficient purity and resistivity that the Li remains unassociated with impurities or acceptors, then the ion drift rate should yield reasonable values for the diffusion rate of Li in Si. A series of measurements using 1000 ohm-cm vacuum-grown floating-zone Si gave a diffusion constant of $6 \times 10^{-4} \exp(-0.61q/kT)$ cm²/sec,

¹⁷ F. M. Smits, Proc. Inst. Radio Engrs. **46**, 1049 (1958).

using the data from these measurements alone (see Fig. 8, which will be described further in a subsequent section). This is to be compared to a value of $23 \times 10^{-4} \times \exp(-0.66q/kT)$ cm²/sec obtained from high-temperature measurements¹⁸ and $23 \times 10^{-4} \exp(-0.72q/kT)$ cm²/sec obtained from low-temperature measurements.¹⁹ The present data and those of reference 18 can be joined by a straight line which falls within the experimental error of both the present measurements and those of reference 18.

8. If the ion drift rate does indeed measure the diffusion constant of the Li, then it should be possible, at these temperatures, to decrease the drift rate by using lower resistivity silicon such that ion pairing effects are significant,¹ or by using silicon of high oxygen content such that Li-O complex formation is significant.³ Both of these effects have been observed, and will be noted in the next section.

MEASUREMENT OF DIFFUSION RATES WITH ION DRIFT

The ion drift technique is inherently very sensitive for measuring drift and hence diffusion rates both because of the very high near-breakdown field which can be used and because the measuring rod is so short, being the width of an $n-p$ junction. (The measuring rod has a slight further virtue in that it becomes longer as the experiment proceeds, permitting the convenient measurement of a wide range of diffusion rates in a single experiment.) With Li in Si, we commonly measure diffusion rates over four decades in a single experiment by varying the temperature. This is illustrated in Fig. 8 which gives preliminary results from such a measurement in crucible grown Si which contained about 10^{18} oxygen atoms/cc from 9μ infrared absorption measurements.²⁰ The diffusion rate at 25°C was derived from the data illustrated in Fig. 9, which is a measure of the

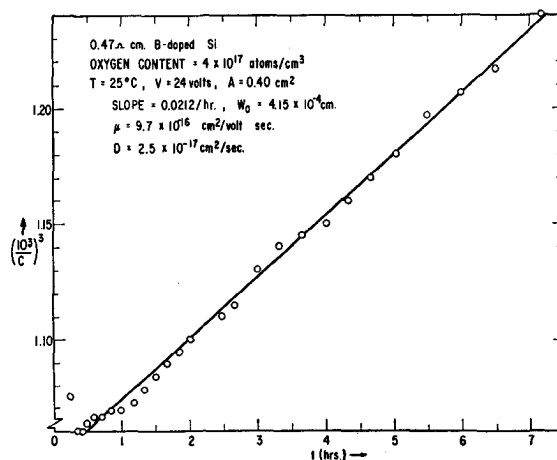


FIG. 9. Initial intrinsic region growth at 25°C .

¹⁸ C. S. Fuller and J. C. Severiens, Phys. Rev. **96**, 21 (1954).

¹⁹ J. P. Maita, J. Phys. Chem. Solids **4**, 68 (1958).

²⁰ W. Kaiser and P. H. Keck, J. Appl. Phys. **28**, 882 (1957).

initial junction growth when the measuring rod was shortest and the measurement most sensitive. From the appearance of these data it is estimated that a diffusion constant as small as 10^{-18} cm²/sec could be measured with good accuracy. Figure 8 also includes data from floating-zone Si of 1000 ohm-cm resistivity, which are indicative of the diffusion rate of free Li⁺ in Si.

The results described in the preceding paragraphs are intended only to be illustrative of the use of ion drift in diffusion measurements. They are neither final nor complete, and estimation of errors and reconciliation with other experiments have not been completed. Final results and conclusions will be the subject of future reports. The general features—in particular, the effect of the oxygen in decreasing the diffusion rate, are real and are in general agreement with previous findings.³ Similar effects, as suggested by the single point for 3 ohm-cm Si, should be observed in floating-zone Si of higher acceptor concentration, such that ion-pair relaxation times are within the period of the experiment, and will be used to measure ion pairing phenomena.¹ By appropriate choice of resistivity and temperature it should also be possible to measure the relaxation times for such pairing and complexing phenomena; present data show such effects but they have not yet been made quantitative.

The large effect of oxygen upon the diffusion rate, especially at low temperatures, combined with the sensitivity of the ion drift technique, should make it useful for measuring oxygen content at low concentrations. Since the model for Li-O interaction is simple and is felt to be well understood,³ confidence in the results should be correspondingly high. We estimate that an oxygen concentration as small as 10^{15} atmos/cc should be accurately measurable by drifting at a temperature of 0°C.

Because the ion drift rate is measured at low concentrations of the diffusant (about 10^{13} /cc in 1000 ohm-cm Si) it can reveal chemical interactions between the diffusant and constituents which may themselves be present only in very low concentration, for example because of limited solubility.

INTRINSIC REGION FORMATION FOR DEVICES

In a diode structure, the incorporation of an intrinsic region by ion drift leads to a lower capacitance and a lower electric field for a given applied voltage. For example, a diode having a breakdown voltage in excess

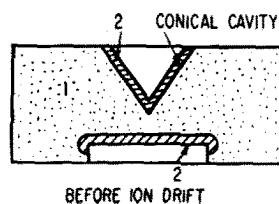


FIG. 10. Formation of analog transistor; configuration after initial diffusion. Region 1: *p*-type Si; reg. 2: *n*-type Si from Li diffusion.

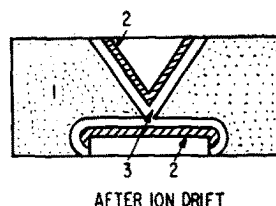


FIG. 11. Formation of analog transistor; configuration after ion drift. Region 1: *p*-type Si; reg. 2: *n*-type Si; reg. 3: intrinsic Si from ion drift.

of 4 kv has been produced using Si with a resistivity of 20 ohm-cm. There would seem to be no inherent limit to the PIV that can be achieved, though the forward characteristic would of course suffer if the junction width exceeded the diffusion length. Also, at high PIV, surface breakdown becomes a problem (the 4 kv unit was immersed in silicone oil to prevent air breakdown). In a similar manner, the decreased capacitance resulting from ion drift might be advantageously used in improving high frequency response, for example, by the use of ion drift in achieving PNIP or NPIN transistor structures.

A more fascinating function of ion drift is its use to produce complex microgeometries. For example, its use permits the fabrication of true analog transistor structures, in which a space-charge limited current flows through an intrinsic semiconducting medium under the control of a grid, exactly as in a vacuum tube. Thyatron analogs are also possible by combining electron and hole currents in the same structure. One method for achieving an analog transistor structure is illustrated in Fig. 10 and Fig. 11. The former illustrates the geometry subsequent to the diffusion of the mobile impurity; the latter illustrates the geometry after sufficient ion drift to produce an aperture in the intervening low-resistivity semiconductor. By applying appropriate biases, as in Fig. 12, one of the initially diffused regions becomes the source (analogous to the cathode), the other initially diffused region becomes the drain (analogous to the anode), and the intervening low-resistivity region with its aperture becomes the grid. Several such devices have been constructed; one exhibited an input resistance of 6 megohms, a power gain of 17 db and a voltage gain of 4. In addition to the advantage of high input impedance, such a device has the further advantage that its properties are essentially independent of temperature, below the temperature at which diffusion destroys the geometry. For good frequency response, a different geometry with a smaller input capacitance would be required. In principle, the presence of the field in the drift region would improve the frequency response through its decrease of the transit time, but the high input capacitance prevents this advantage from being realized here.

One would expect to observe space-charge limited emission in such analog transistor structures.^{21,22} In a *p-i-p* structure, made by Li-ion drift and with a grid

²¹ N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals*, (Oxford University Press, 1940), p. 172.

²² A. Rose, *Phys. Rev.* **97**, 1538 (1955).

aperture which happened to be too large to exhibit control, it appeared that space-charge limited emission was observed. The current varied as V^2 and the current had a magnitude of 1 ma with 1 volt applied. This is consistent with space-charge limited emission for an area of 0.01 cm² and a separation of 0.004 cm, these values being reasonable though not independently measured for this unit. In another unit with smaller grid aperture, such that the unit exhibited power gain, the current depended linearly on voltage at lower voltages and increased slightly more slowly with voltage at higher voltages; this observation is not understood but has not been pursued further.

No extensive study of the effect of the Li diffusion and ion drift upon carrier lifetime has been made nor have any special efforts been made to keep the lifetime high. Carrier lifetimes at least as high as 160 μsec, and also as short as 3 μsec, (in drifted units without *B* skin) have been observed by the diode recovery method.²³ In another unit which was subjected to an initial *B* diffusion step at 1150°C as described in a previous section, the lifetime was about 3 μsec, with forward and reverse characteristics in reasonable agreement with this lifetime. Since Li is a shallow donor, it would not by itself be expected to decrease the lifetime,²³ but whatever is responsible for the heat treatment to which reference has previously been made could also affect the lifetime, as could high-temperature heat cycles.²³ With Li, it is possible to avoid high-temperature heat cycles, and it may hence prove more feasible to retain high lifetimes with this diffusant. Reasonable lifetime would be of importance in obtaining a good forward characteristic in a high-voltage *p-i-n* junction; it would be of less importance in an analog transistor because here the field makes transit times small.

The useful life of ion drift devices depends upon many factors. High-temperature storage life without applied potential is limited by the time it takes for diffusion to smear out the intrinsic region. High-temperature life with applied field depends on the time it takes the Li⁺ available in the source to all drift through the unit. In an analog structure, the grid aperture must not change appreciably, imposing a more stringent limitation on allowable drift during the useful life, though geometries are possible which minimize this problem by use of a nonuniform initial distri-

bution of what would in the present examples be the immobile acceptor ions. In Li-Si diodes using oxygen to slow the Li diffusion (see previous section), reasonable operating lifetimes with voltage applied at temperatures up to 125°C and reasonable storage lifetimes without applied voltage at temperatures up to 75°C should be attainable. Higher operating temperatures would require the use of a slower diffusant or a different host lattice, subject of course to the limitation that drift must occur at a temperature such that an *n-p* junction exists. The number of possible choices for such other materials is enlarged by the fact that they need not be of high purity.

CONCLUDING REMARKS

The primary intent of this paper has been to describe and analyze a new technique for producing an intrinsic region in semiconductors. Data have been presented to illustrate the features of the kinetics and to experimentally confirm the results of the analysis. The significance of the method as a research tool and also its possible usefulness in the device area have been briefly described and illustrated.

ACKNOWLEDGMENTS

The author is deeply appreciative of many ideas originating in discussions with other members of the Semiconductors Studies Section of the General Electric Research Laboratory, particularly R. N. Hall, F. S. Ham, E. O. Kane, and A. G. Tweet. For the experimental results, he is largely indebted to the capable efforts of D. J. Locke.

APPENDIX

This appendix will present an analysis of the increase in junction width with ion drift for constant applied voltage, *V*, for a mobile donor ion of concentration *N*(*x*) diffused into a crystal having a uniform concentration, *N_A*, of immobile acceptor ions.

Approximation for Long *t* and *W* ≫ *L*

The starting point will be Eq. (10) of the text:

$$\int E \mu dt \simeq L \{ (c^2/a^2) \exp[(c^2 - a^2)/4D_0 t_0] - 1 \} + a - c$$

$$\simeq b - c - L \{ 1 - (c^2/b^2) \exp[(c^2 - b^2)/4D_0 t_0] \}. \quad (A1)$$

Although *E* can in general be obtained from *V* only through a detailed knowledge of intrinsic region width and space charge region distribution, some simplification results at long *t* because the space charge width becomes negligible relative to the intrinsic width. This occurs both because the intrinsic region becomes constantly wider and because the space charge region becomes constantly narrower, the latter resulting from the fact that the required space charge is equal to

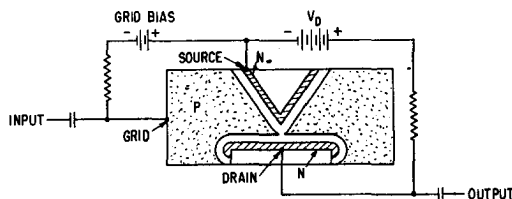


FIG. 12. Circuit for analog transistor.

²³ G. Bemski, Proc. Inst. Radio Engrs. 46, 990 (1958), and references cited therein.

voltage times capacitance and hence decreases as the capacitance decreases. The early stages of growth can be avoided by dealing with the differential form of Eq. (A1), which gives μ in terms of the growth rate at long t . For somewhat shorter t , the differential form can be integrated and the integration constant evaluated from the data at long t . The resulting relation between junction width and time can be compared with experiment to check the range of validity of the simplifying assumptions.

From the first and third equalities of Eq. (A1), for $(b^2 - c^2) \gg 4D_0 t_0$ (which is essentially for $W \gg L$),

$$\int E \mu dt \simeq b - c - L. \quad (\text{A2})$$

Approximating E by V/W ,

$$\int (V/W) \mu dt \simeq b - c - L. \quad (\text{A3})$$

The term equal to c can be eliminated by using the second and third equalities of Eq. (A1), subject to the previous approximations:

$$W/L \simeq (c^2/a^2) \exp[(c^2 - a^2)/4D_0 t_0]. \quad (\text{A4})$$

Since $L = 2D_0 t_0/c$ [from Eq. (4)], this yields

$$(c - a) = L \ln(W/L) \quad (\text{A5})$$

so that, from Eq. (A3), and also noting that $W = b - a$,

$$\int (V/W) \mu dt = W - L - L \ln(W/L). \quad (\text{A6})$$

Differentiating, there is obtained

$$dW/dt = V\mu/W(1 - L/W) \quad (\text{A7})$$

giving

$$d(W^2)/dt = 2V\mu/(1 - L/W), \quad (\text{A8})$$

or

$$d(W^2)/dt \simeq 2V\mu \text{ for } W \gg L. \quad (\text{A9})$$

L is related to the space charge width, W_0 , of the initial gradient-type junction by $L = (W_0^3 N_A / 12\kappa V)$, obtained in the usual fashion by integrating the field across the initial junction.

Equation (A7) can be integrated, giving

$$W^2 - 2LW = 2V\mu t + K \quad (\text{A10})$$

where K , the integration constant, must be determined experimentally because the integral is wrong at short t , when $E \neq (V/W)$.

In Eqs. (A7) and (A8), the L in the denominator results from the fact that the intrinsic region grows at a finite rate toward the side of high Li^+ concentration, as well as in the direction of low Li^+ concentration where most of the growth takes place.

The above expressions will be correct only when diffusion can be neglected relative to drift in the field. In cases of strong ion pairing or small fields this condition might not be fulfilled, and dW/dt could be appreciably reduced or even zero. This would arise because the boundary of the intrinsic region on the high Li^+ side would move continuously toward the other boundary because of Li^+ diffusion.

Approximation for Short t and $W \ll L$

From Eq. (8) of the text,

$$\int E \mu dt \simeq W^2/8L. \quad (\text{A11})$$

But $L = N_A/(dN_D/dx)|_{x=c}$ [see Eq. (4)], and the gradient at $x=c$ can be written in terms of the space charge width prior to ion drift, W_0 , by integration of Poisson's equation, as $(dN_D/dx)|_{x=c} = 12\kappa V/W_0^3$, where κ is the dielectric constant and V is the voltage across the junction, giving

$$\int E \mu dt \simeq 3W^2 \kappa V / 2N_A W_0^3. \quad (\text{A12})$$

From now on we wish to distinguish between the intrinsic region width, W_I , the space-charge region width, W_{sc} , and the total junction width, $W = W_I + W_{sc}$, so that Eq. (A12) becomes

$$E_I \mu dt \simeq 3W_I^2 \kappa V / 2N_A W_0^3. \quad (\text{A13})$$

We must next evaluate E_I/V as $f(W_I, W_{sc})$ and then rewrite $f(W_I, W_{sc})$ as $F(W, W_0)$. To evaluate E_I/V we approximate the space charge by a linear gradient with half of the space charge width and intrinsic region width on either side, as in Fig. 13. There is obtained

$$E(l) = \int \rho dl / \kappa = (l \nabla N / 2\kappa)(W_I + W_{sc} - l), \quad (\text{A14})$$

and

$$E_{\max} = (W_{sc} \nabla N / 4\kappa)(W_I + W_{sc}/2). \quad (\text{A15})$$

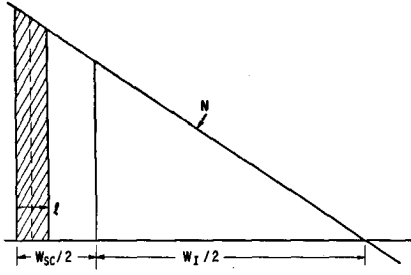
This E_{\max} is the E which exists throughout the intrinsic region and is hence the E_I to be used in our expression for E_I/V . V is found through a further integration of Edl :

$$V = (W_{sc} \nabla N / 4)(W_{sc} W_I + W_I^2 + W_{sc}^2 / 3). \quad (\text{A16})$$

Dividing Eq. (A16) by Eq. (A15) and noting that $W_{sc} = W - W_I$,

$$3V/2E_I = W + W_I - WW_I/(W + W_I); \quad (\text{A17})$$

W_I can be eliminated by noting that at $t=0$, $V = \nabla N W_0^3 / 12\kappa$ (from the usual expression for a gradient-type junction, as obtained from integrating Poisson's equation). Using this value for V in Eq. (A16)


 FIG. 13. Approximate impurity distribution at short t .

and eliminating W_{sc} as before there is obtained

$$W_I = (W^3 - W_0^3)^{1/3}. \quad (\text{A18})$$

Using Eqs. (A17) and (A18) with Eq. (A13), there is obtained for $x \equiv W/W_0$,

$$\frac{dx}{dt} = (N_{A\mu}/\kappa) (x^3 - 1)^{1/3} \{ 2x^2 [x + (x^3 - 1)^{1/3}] - (x^3 - 1)^{1/3} x / [x + (x^3 - 1)^{1/3}] \} \quad (\text{A19})$$

which, for large x , becomes

$$\frac{dx}{dt} \simeq N_{A\mu} / 3x^2 \kappa, \quad (\text{A20})$$

or

$$d(x^3)/dt \simeq N_{A\mu} / \kappa. \quad (\text{A21})$$

According to Eq. (A19), as x approaches unity, dx/dt approaches zero. But the above approximations are not valid in this region, for they neglect the initial transport of ions by the field throughout the space charge region. It will be shown subsequently that the exact solution for $d(x^3)/dt$ at $t=0$ is just the same as that given by Eq. (A21). Since our experiments do not suggest any S-shaped character to the true behavior, it seems reasonable that Eq. (A21) is obeyed throughout the initial range, in which case it can be integrated to give

$$x^3 = N_{A\mu} t / \kappa + 1, \quad (\text{A22})$$

the one being necessary to make x equal to one at the origin.

A plot of W^2 versus time will hence have an initial region where the curvature is negative; in this region the junction width is less than a few L , where L is defined in connection with Eq. (4). At this stage the junction is increasing in width toward both the Li-rich and Li-deficient sides, with an ever-increasing amount of Li^+ transport being required for a given incremental increase in junction width. Finally, when the junction width greatly exceeds L , the curvature becomes zero, in accordance with Eqs. (A8) and (A9). In this region growth is primarily toward the Li-deficient side, with each increment of junction width requiring essentially the same amount of Li^+ transport.

Exact Solution at $t=0$, for $W \ll L$

We shall consider the simplified case where the initial Li^+ concentration near the junction can be approximated by a linear gradient. Near $t=0$, the Li^+

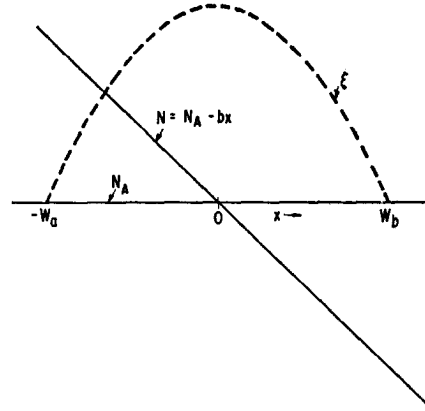


FIG. 14. Initial field and impurity concentrations.

concentration as a function of time will be approximated by the first two terms of a power series. The field and voltage will then be determined as a function of time near $t=0$, and from them it will be possible to find dW/dt at $t=0$.

In accordance with Fig. 14,

$$N(x,t) |_{t=0} = N_A - bx. \quad (\text{A23})$$

Near $t=0$, the first two terms of a power series for N gives

$$N(x,t) = N(x,0) + t(dN/dt)(x,0). \quad (\text{A24})$$

But at any x ,

$$\frac{dN}{dt} = -E\mu \frac{dN}{dx} + D \frac{d^2N}{dx^2} - N\mu \frac{dE}{dx}. \quad (\text{A25})$$

Noting also that in this particular case $d^2N/dx^2=0$, Eq. (A24) becomes

$$N(x,t) = N_A - bx + t\mu [bE - (dE/dx)(N_A - bx)]. \quad (\text{A26})$$

For E , we can use the initial field, which for this gradient-type junction is $(1/\kappa)(bW_0^2/8 - bx^2/2)$, where b here is the gradient, giving

$$N(x,t) = N_A - bx + (t\mu/\kappa) \times [b^2W_0^2/8 + bxN_A - 3bx/2]. \quad (\text{A27})$$

Knowing $N(x,t)$, it is possible to find E and V . To find E , one integrates the charge density:

$$E = \int \rho dx = \int (N - N_A) dx. \quad (\text{A28})$$

Making use of the boundary condition that $E=0$ at $x=W_b$, this gives

$$\kappa E = -bx^2/2 + bW_b^2/2 + (t\mu/\kappa) [(b^2W_0^2/8)(x - W_b) + N_A b(x^2/2 - W_b^2/2) - b^2(x^3/2 - W_b^3/2)] \quad (\text{A29})$$

with an identical expression, changed only by the substitution of $(-W_a)$ for W_b , corresponding to the boundary condition $E=0$ at $x=(-W_a)$.

To find V , E is integrated from $(-W_a)$ to W_b , giving

$$V = bW_a^3/3 + bW_b^3/3 + (t\mu/\kappa)[(b^2W_0^2/16)(W_a^2 - W_b^2) - (N_A b/3)(W_a^3 + W_b^3) - (3b^2/8)(W_a^4 - W_b^4)]. \quad (\text{A30})$$

To find dW/dt , the differential of Eq. (A30) is next taken, noting that V is constant:

$$\begin{aligned} 0 = & bW_a^2 dW_a + bW_b^2 dW_b \\ & + (t\mu/\kappa)[(b^2W_0^2/8)(W_a dW_a - W_b dW_b) \\ & - N_A b(W_a^2 dW_a + W_b^2 dW_b) \\ & - (3b^2/2)(W_a^3 dW_a - W_b^3 dW_b)] \\ & + (\mu dt/\kappa)[(b^2W_0^2/16)(W_a^2 - W_b^2) \\ & - (N_A b/3)(W_a^3 + W_b^3) - (3b^2/8)(W_a^4 - W_b^4)]. \quad (\text{A31}) \end{aligned}$$

Initially, $W_a = W_b = W_0/2$, $dW_a = dW_b = dW/2$, and $t=0$, giving

$$0 = bW_0^2 dW/4 - \mu N_A b W_0^3 dt/12\kappa. \quad (\text{A32})$$

This leads to

$$(dW/dt)|_{t=0} = N_A \mu W_0/3\kappa, \quad (\text{A33})$$

and since $d(W^3)/dt = 3W^2 dW$, and for $x \equiv W/W_0$,

$$[d(x^3)/dt]|_{t=0} = N_A \mu/\kappa, \quad (\text{A34})$$

which is the same as Eq. (A21), as noted earlier.

It is also possible to find the ratio of the initial slope, $d(W^2)/dt|_{t=0}$, to the final slope given by Eq. (A9):

$$(d(W^2)/dt)|_{t=0} = 2W dW/dt|_{t=0} = 2N_A \mu W_0^2/3\kappa; \quad (\text{A35})$$

$$(d(W^2)/dt)|_{t=\infty} = 2V\mu = 2\mu b W_0^3/12\kappa. \quad (\text{A36})$$

Noting that $b = N_A/L$, this gives

$$\text{initial slope/final slope} = 4L/W_0. \quad (\text{A37})$$

This will be valid, of course, only where W_0 is initially small relative to L , in accordance with the initial assumptions of this section, but it indicates that the change in slope will become decreasingly noticeable as W_0 increases. W_0 will be greater if the resistivity of the starting material is greater or if the applied voltage is greater.

Approximation for $W_0 \gg L$

In high-resistivity material, it is possible for W_0 to exceed L for voltages normally applied. In this case, the appropriate starting point becomes Eq. (10) of the text, which for $W_0 \gg L$ becomes

$$\int E \mu dt \simeq W \quad (\text{A38})$$

giving

$$d(W^2)/dt \simeq 2V\mu \text{ at long } t. \quad (\text{A39})$$

As before, for short t when W_0 is comparable with W , E cannot be approximated by V/W . A solution in this range would require a procedure similar to that used in obtaining Eq. (A22), except that a linear gradient approximation such as the one of Fig. 13 is not appropriate when $W_0 \gg L$. Because of this added complication it has not yet proved feasible in the present case to find the slope analytically at short t . In view of experimental results such as those of Fig. 6, and in view of the trend suggested by Eq. (A37), it is tentatively assumed that the initial slope is the same as the final slope of Eq. (A39).