

for cadmium is very similar to that found for zinc¹ where θ_0 (elastic) is 328°K, and θ_0 (calorimetric) is 309°K. Although the reason for the discrepancies is not certain it still seems possible that they may arise from the difficulty of interpreting the low-temperature heat ca-

capacity of highly anisotropic metals. For both zinc and cadmium there is a sizeable T^5 lattice contribution as well as the large electronic heat capacity; both of these factors must be taken into account carefully in obtaining the T^3 contribution that determines θ_0 .

Diffusion Rate of Li in Si at Low Temperatures*

E. M. PELL

General Electric Research Laboratory, Schenectady, New York

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The method of ion drift in the electric field of an n - p junction has been used to measure the diffusion constant of Li in Si between 25°C and 125°C, taking particular care to avoid chemical and electrical interactions which might affect the results. When these data are combined with previous high-temperature data, there is obtained $D = (2.5 \pm 0.2) \times 10^{-3} \exp[-(0.655 \pm 0.01)e/kT]$ cm²/sec, the data extending over eight decades in D . The results are compared with those from ion-pair relaxation experiments, and it is shown that the latter are consistent with the ion-drift results.

INTRODUCTION

THE method of ion drift in the electric field of a reverse-biased n - p junction¹ offers a sensitive technique, based on a simple model, for diffusion measurements at low temperatures. This method can be adapted to the measurement of the diffusion rate of free Li⁺ in Si through the use of techniques which minimize or eliminate possible interactions between the Li⁺ and other constituents present in the Si.

Because of the simplicity of the technique and of the model upon which it is based, the results should be highly reliable. They can be compared with values deduced from previous measurements² in this temperature range which are based on a particular model³ of ion-pairing kinetics. Such a comparison is of particular interest inasmuch as two different approaches have been suggested^{3,4} to the analysis of such diffusion-limited "precipitation" (or, in this case, ion-pair recombination), these approaches leading to different values for the diffusion constant when applied to Maita's data. In essence, the former³ approach visualizes the recombination as correlated, with each Li⁺ to be associated uniquely with a particular acceptor, while the latter⁴ approach considers the Li⁺ ions to be initially randomly located, with nothing to inhibit their motion from the neighborhood of one acceptor to another.

I. Ion-Drift Measurements

Experimental Method

In the present experiments, the diffusion constant is deduced from the rate at which the Li⁺ ions drift in the electric field of a reverse-biased p - n junction. The p - n junction is prepared in a preliminary step by diffusing Li into the surface of a piece of p -type Si. The drift rate of the Li⁺ ions, at a given temperature, is determined by measuring the rate of change of the capacitance of the junction. Complete details, with a full discussion of the experimental techniques, is given in reference 1, together with a description of the surface treatment normally used in making measurements on high-resistivity Si such as that used here.

Effects of Li-Impurity Reactions

At the low Li concentrations and low diffusion temperatures used in this experiment, it is possible for Li acceptor, Li oxygen, Li dislocation, or perhaps even other unknown interactions to affect the diffusion rate. Before one can be sure that the results are descriptive of free Li, these possibilities must be eliminated.

The presence of any such interaction will generally lead to an activation energy for diffusion which is different from that of free Li; however, such an interaction should be absent at high temperatures because of the relatively small binding energies involved. The facts that the present low-temperature data fall along a straight line (as shown later in Fig. 2) and that this line extrapolates through the previously determined high-temperature diffusion data⁵ serve, therefore, as general

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¹ E. M. Pell, J. Appl. Phys. **31**, 291 (1960).

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

³ H. Reiss, C. S. Fuller, and F. J. Morin, Bell System Tech. J. **35**, 535 (1956).

⁴ F. S. Ham, J. Phys. Chem. Solids **6**, 335 (1958).

⁵ C. S. Fuller and J. C. Severiens, Phys. Rev. **96**, 21 (1954); also, E. M. Pell, Phys. Rev. **119**, 1014 (1960).

arguments to indicate that such interactions are small or absent in these data.

Specific interactions have been further excluded through subsidiary experiments. Consider first Li-acceptor interactions. Since the predominant acceptor in our samples was boron, only this need be considered. In a sample containing 10^{17} B atoms/cm³, the diffusion rate at room temperature was found to be reduced to about 7% of the value indicated in Fig. 2. Equation (9.5) of reference 3 indicates that if the boron concentration is reduced from this value of 10^{17} /cm³ to the value of 10^{13} atoms/cm³ used in obtaining the data of Fig. 2, the fraction of atoms associated is reduced to about 2% at room temperature and less at higher temperatures. This can be neglected.

In the case of oxygen, it has been found that 10^{18} oxygen atoms/cm³ (as determined by the 9μ infrared resonance) reduce the effective diffusion rate to about 0.1% of that given in Fig. 2 for room temperature. This leads to a value of $C \approx 10^{18}$ cm⁻³ at room temperature in the expression^{6,7}

$$D_{\text{eff}} = \left\{ \frac{n-N-C}{2n} + \left[\left(\frac{n-N-C}{2n} \right)^2 + \frac{C}{n} \right]^{\frac{1}{2}} \right\} D, \quad (4)$$

where $n = [\text{Li}^+] + [\text{LiO}^+]$ and $N = [\text{O}] + [\text{LiO}^+]$, the brackets denoting concentrations. (This value was also obtained in earlier precipitation experiments.⁷) For $n \ll N$, Eq. (4) reduces to

$$D_{\text{eff}} = D / (1 + N/C).$$

The best estimate of the oxygen concentration in the vacuum grown floating zone silicon which we used is about 10^{15} atoms/cm³,⁷ which would lead to $D_{\text{eff}}/D = \frac{1}{2}$ at room temperature, and very nearly unity at 50°C where C is greater by roughly a decade. Thus, from this argument alone one could anticipate some decrease in D at room temperature but no decrease at higher temperatures. The anticipated possible decrease at room temperature is reduced from 50% to less than 20% if one also considers the kinetics of the reaction. Thus, the time constant, τ , for the Li-O reaction can be estimated by use of the formula $1/\tau = 4\pi DNr$,⁴ where D is the diffusion constant, N is the concentration of the trapping site (in this case oxygen) and r is its radius (which can be estimated as roughly a lattice constant). In the present instance, this gives a τ of about 600 hours at room temperature. The median point of our drift measurements was about 250 hours, at which point the reaction would have gone to only about 34% of completion, and the decrease in D at this point would then be about $50\% \times 34\%$, or about 17%.

⁶ H. Reiss, Report of the American Institute of Mining and Metallurgical Engineers Symposium on Properties of Elemental and Compound Semiconductors, Boston, August, 1959 (Interscience Publishers, Inc., New York, to be published).

⁷ E. M. Pell, *International Conference on Solid-State Physics in Electronics and Telecommunications, Brussels, 1958* (Academic Press, Inc., New York, 1960), Vol. I.

The possible effects of dislocations are difficult to assess theoretically. An experimental approach was accordingly tried. In addition to the drift experiments in the floating-zone Si, which contained about 10^4 dislocations/cm² as determined from etch-pit counts using the Dash technique,⁸ two experiments were performed using dislocation-free Si vacuum-grown by Dash using his pedestal technique.⁹ The results, as indicated in Fig. 2, were identical with those from the other Si. In addition, two twisted samples were tried, one with a 5° twist having about 6×10^6 dislocations/cm² at the surface used for ion drift, and another with 15° twist having about 3×10^7 dislocations/cm². In the latter sample, the drift rate dropped with time until it was essentially zero; in the former, the drift rate was about $\frac{1}{10}$ of its normal value. In view of the complexity of the problem, particularly resulting from possible effects on the field of the junction and from possible precipitation phenomena, no explanation is offered, nor does it seem worthwhile to pursue the problem with these techniques. The result has been established that in the samples normally used the dislocation density was insufficient to affect the results, but that dislocation densities 600 times as great could have a profound effect.

Temperature Determination

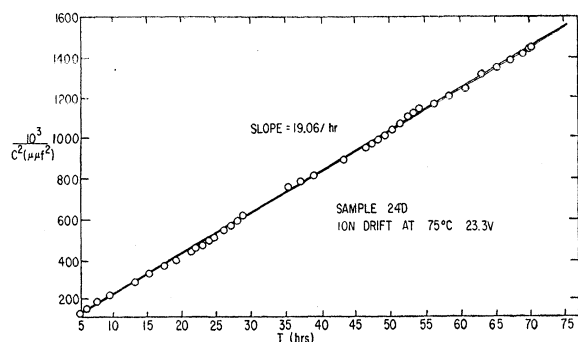
For room-temperature experiments, the room temperature near the apparatus was read periodically; it varied typically over an 8°C range. These values were averaged, weighting them in proportion to the time spent at each T . The result is felt to be accurate to within $\pm 1\frac{1}{2}$ °C. At higher temperatures, the sample was enclosed in a small oven with a thermistor controller having a reading accuracy of about $\frac{1}{2}$ °C, with overnight drifts not in excess of this. This was calibrated against an annealed Pt-Pt 10% Rh thermocouple in contact with the surface of the samples, with the same gas flow as used in the drift experiments. (The gas flow was found to cause a 0.7°C drop in sample temperature at 75°C.) The over-all accuracy of these higher temperature measurements is felt to be ± 1 °C.

Junction Voltage

Because of the high bulk resistivity of the Si used in these experiments, the observed saturation currents at the higher temperatures could result in sizeable voltage drops through the samples and hence in junction voltages lower than those measured. By means of experimentally determined C - V calibration curves and special runs at low sample voltages, first-order corrections to the junction voltage were determined at 125°C through measurements of changes in junction capacitance with sample temperature, these changes being rapid relative to changes caused by ion drift. At lower temperatures,

⁸ W. C. Dash, J. Appl. Phys. **27**, 1193 (1956).

⁹ W. C. Dash, J. Appl. Phys. **29**, 736 (1958).

FIG. 1. Variation of $1/C^2$ with time in typical sample.

where the capacitance changes were too small to give accurate results, the corrections determined at 125°C were scaled down in proportion to the measured sample current. In addition, a small correction was made for the estimated built-in junction voltage.

The sample voltage drop determined by the above technique amounted to as much as 71% of the applied voltage at 125°C, 19% at 100°C, 6% at 75°, and 2% at 50°. In some runs, where the leakage currents were lower, the corrections were much less than these. In general, however, the 125°C and 100°C data may contain appreciable errors from this source.

Sample Heat Treatment

The changes in sample resistivity incidental to the surface treatments, as discussed in reference 1, were often considerable. Generally the resistivity increased, the largest measured increase being by a factor of ten. It was noted that the diffusion data from the samples with large resistivity changes showed worse scatter (by a factor of about two). Since these samples were felt to be poorly understood and under poor control, it was arbitrarily decided to exclude all data from samples whose resistivity changed by more than a factor of two.

Junction Areas

The Li-in-oil dispersion showed a slight tendency to pull away from the edges of the sample during the alloying process, and it was therefore not possible to use the bar area as a measure of the junction area. All samples were probed to find the position of the n - p junction at the end of the experiment, and the resulting area was used in the calculations.

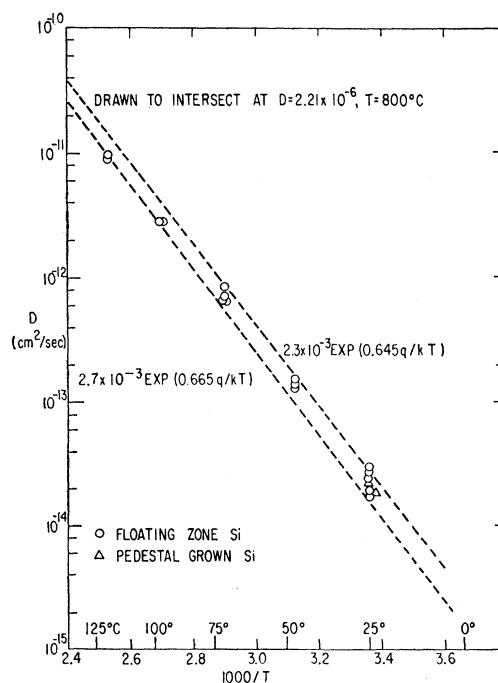
Experimental Results

A typical curve of $1/C^2$ vs time, where C is the junction capacitance, is given in Fig. 1. The calculated diffusion constants for all samples whose resistivities changed by less than a factor of two through heat treatment, corrected for sample voltage drop and built-in junction voltage, are exhibited in Fig. 2. The dotted lines pass through the previous high-temperature data.⁵ Within

the experimental error, the data fall along a straight line, and the slope is consistent with that of the previous high-temperature data. The slight droop at the higher temperatures is attributable to larger relative errors in the junction-voltage correction at these temperatures. The larger degree of scatter at room temperature, especially toward lower D , may be caused by Li-oxygen interactions as discussed previously. The remaining scatter is not understood; it appears to exceed the estimated errors. These rationalizations for the scatter lead one to favor, as the most probable, a curve lying somewhat above the median of those drawn, or a value for D of $2.4 \times 10^{-3} \exp(-0.65q/kT)$ cm²/sec.

II. Comparison with Ion-Pairing Kinetics

The present results yield a D of $(2 \text{ to } 3.5) \times 10^{-14}$ cm²/sec at 27°C, whereas the ion-pairing experiment of Maita² yielded a value of 3.4×10^{-15} cm²/sec at 27°C when used with the model of reference 3. Ham's model,⁴ when applied to the case of ion pairing, predicts a non-exponential behavior; a logarithmic plot of the change in concentration vs time should show an initial time constant, when the ion pairs are initially fully ionized, equal to that predicted by Reiss, but the final time constant should correspond to that calculated by replacing the total acceptor concentration in Reiss' expressions by the net acceptor concentration. Since Maita observes that his ion pairs were 50% ionized at 470°K, they must have been even less completely ionized at his dissociation temperature of 373°K, so that his measured time constant could conceivably correspond to the latter

FIG. 2. Logarithmic plot of diffusion constant vs $1/T$.

stage of Ham's model. Such an interpretation leads to a D of 1.8×10^{-14} cm²/sec at 27°C, in good agreement with the present results.

In an effort to distinguish experimentally between the two models, a series of ion-pair relaxation experiments such as those of Maita's were performed, differing principally in the use of more closely compensated samples and of higher dissociation temperatures (generally 200°C) sufficient to completely dissociate the ion pairs. The use of very close compensation (better than 95% in the p -type Li-B doped vacuum-grown floating zone Si samples described here) should lead to larger and more easily recognized differences between the exponential behavior predicted by Reiss' model and the non-exponential behavior of specified curvature predicted by Ham's model.

The results from such an experiment are given by curve A of Fig. 3. If the Li⁺ ions were distributed completely randomly after the quench, and if the B⁻ ions acted as square-potential-well traps, then dividing the data of curve A by $(1+N/K)$, where N is the instantaneous free B⁻ concentration and K is the final net B⁻ concentration, should result in straight line C (the two lines shown for C correspond to the experimental uncertainty in the initial slope of curve A). Such a division actually results in curve B . Ham's model predicts only that curve B should have equal initial and final slopes and that this slope should be equal to the initial slope of curve A divided by N/K . This is in agreement with the experimental results. Reiss' model of correlated pairing, on the other hand, predicts that the initial slope of curve A should remain constant during the pairing; this would result in a negative curvature for curve B throughout its range. The fact that curve B starts out with a negative curvature suggests that some correlation is present. The fact that the curvature in curve B is far less than the curvature in curve A indicates that a completely uncorrelated approximation is a closer approach to the physical process.

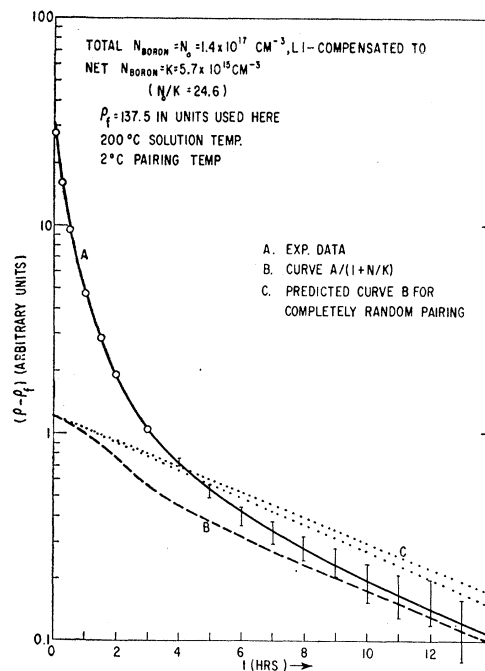


FIG. 3. Ion-pairing kinetics, experiment and theory.

A series of such experiments yields a value for D in accord with the present ion drift results. These experiments and their implications to our understanding of the ion pairing process will be discussed in a subsequent paper.

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