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The application of the loop annealing technique to self diffusion studies in silicon

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The loop annealing technique has been applied to the study of self diffusion in silicon over a wide range of doping concentrations. The results show that the diffusion coefficient decreases as the concentration of n-type dopant decreases and the concentration of p-type dopant increases. At a fixed temperature, the diffusion coefficient is linearly dependent on the electron concentration and this behaviour is in accord with the point defects responsible for self diffusion behaving as acceptors. The values obtained for the self diffusion coefficient in intrinsic material are in good agreement with those obtained by other workers at higher temperatures using profiling techniques and indicate a slight curvature in the Arrhenius plot.

1. Introduction

In the absence of any definitive experiments to determine the mechanism of self diffusion in silicon, conclusions as to whether this is of vacancy or interstitialcy type have been inferred from diffusion data. The variation of the self-diffusion coefficient with doping level provides a means of determining the electronic characteristics of the point defects responsible for diffusion and in principle the diffusion mechanism can be identified by comparing these data with other characteristic data obtained, for example, by electron paramagnetic resonance techniques.

Radiotracer studies of self diffusion in silicon are relatively difficult because of the short half life of the Si^{31} isotope and only a limited amount of data are currently available. Both Ghoshtagore [1] and Fairfield and Masters [2] found that the self diffusion coefficient was greater in n-type silicon than in intrinsic material and this result suggests that the point defects are behaving as acceptors. In p-type material Ghoshtagore obtained a lower value of the diffusion coefficient relative to intrinsic material and this result too is in accord with the acceptor model. However, Fairfield and Masters found that the diffusion coefficient was greater in p-type material than in intrinsic material and they suggested that the enhanced diffusion is caused by the more rapid migration of the boron atoms according to a model proposed by Hoffman [3]. Both these authors discussed their results in terms of a vacancy mechanism but Chik [4] has reanalysed the data of Fairfield and Masters and concludes that the point defects are amphoteric and suggests that they are, in fact, interstitials.

It is apparent, therefore, that not only are the basic data inconclusive as regards the electronic nature of the point defects but that much more extensive data are necessary to permit an identification of the point defects in terms of vacancies or interstitials. The present paper describes experiments in which the annealing kinetics of secondary defects, in this case dislocation loops, have been investigated and applied to the study of self diffusion in silicon. This is a relatively simple technique which has been applied successfully to self diffusion measurement in aluminium and copper [5, 6] and in the present case a systematic set of data on the temperature and impurity concentration dependence of diffusion have been obtained.

2. Experimental

The starting materials used in this investigation

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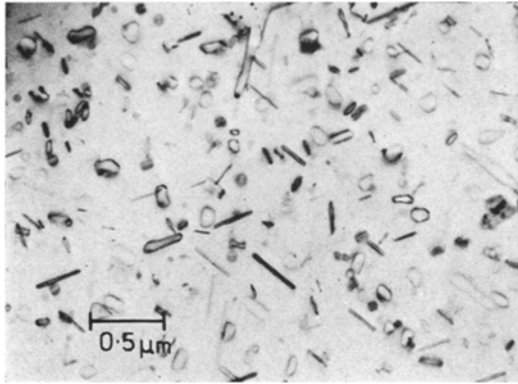

Figure 1 Dislocation loops and dipoles in ion-irradiated silicon bulk annealed for 30 min at 950°C.

were Czochralski single crystal silicon slices of (1 1 1) orientation. The phosphorus doped n-type slices were of nominal resistivity 0.005, 0.01 and 200 Ωcm and the boron doped p-type slices had resistivities of 0.005, 0.008, 0.01 and 5 Ωcm. The dislocation loops were formed from the radiation damage produced by bombarding the polished surfaces of the slices at room temperature with 110 keV Ne ions and the total dose was in the range 10^{14} to 10^{15} cm^{-2}. Discs of 3 mm diameter were ultrasonically cut from the slices and chemically thinned towards the damaged surface by the usual jet thinning technique. An examination in the electron microscope of the bombarded surface regions showed the material to be in the amorphous state but large dislocation loops (Fig. 1) were observed in specimens which had been annealed for 30 min at 950°C in nitrogen prior to chemical thinning. After being examined in the electron microscope, the thinned discs were annealed in a silica tube horizontal furnace in a vacuum of 10^{-5} Torr for various time periods in the temperature range 970 to 1070°C and the same area re-examined in the microscope after each anneal. It was found that the loops shrank during annealing and a plot of loop radius versus annealing time was obtained for each specimen. The annealing temperature was controlled to $\pm$ 2°C and in order to avoid any errors due to slight temperature variations, specimens of each resistivity were annealed together.

3. Analysis

A determination of self diffusion coefficients from the annealing kinetics of secondary defects has been made by a number of workers [5, 6] who have demonstrated the general validity of the technique. Dislocation loops shrink through the diffusion of point defects between the loop and the foil surface and the driving force for the process is provided by the self energy of the dislocation loops. The prismatic loops studied in this investigation have been shown to be of extrinsic character [7] and, therefore, shrink by either the diffusion of interstitial atoms from the loop to the foil surface or by the diffusion of vacancies from the surface to the loop, the nature of the diffusing species being governed by the self diffusion mechanism.

3.1. Interstitialcy self-diffusion mechanism

If interstitials are the mobile species, then the rate of shrinkage of a prismatic loop of radius r is given by

$$\frac{\mathrm{d}r}{\mathrm{d}t} = -\frac{\pi D_{\mathrm{S}}}{f_{\mathrm{I}} b \ln(2s/\boldsymbol{b})}\left[\frac{C_{\mathrm{L}}}{C_0} - 1\right] \quad (1)$$

where D_{S} is the coefficient of self-diffusion, f_{I} is the correlation factor (equal to 0.73 for interstitialcy diffusion in the diamond cubic lattice [8]), s is half the foil thickness, $\boldsymbol{b}$ is the Burgers vector, C_{L} is the interstitial concentration in equilibrium with the loop and C_0 is the equilibrium interstitial concentration.

The interstitial concentration in equilibrium with the loop, C_{L}, is given by

$$\frac{C_{\mathrm{L}}}{C_0} = \exp\left(\frac{\Delta F}{kT}\right) \quad (2)$$

where ΔF is the change in the energy of the loop per emitted interstitial and the total self energy F of a dislocation loop is given by [9]

$$F = \frac{G\boldsymbol{b}^2 r}{2(1-\sigma)}\left[\ln\frac{8r}{\boldsymbol{b}} - 2 + \frac{(3-2\sigma)}{4(1-\sigma)}\right] \quad (3)$$

where G is the shear modulus and σ is Poisson's ratio. The change in energy per emitted interstitial $\Delta F(= \mathrm{d}F/\mathrm{d}n)$ can thus be obtained by making use of the fact that the number of interstitials, n, contained within the loop is given by

$$n = 2\pi r^2/B^2 \quad (4)$$

where B^2 is the atomic cross-section in the (1 1 1) plane.

It was shown by Silcox and Whelan [10] that the term in the square brackets of Equation 1 can be approximated by $\alpha\boldsymbol{b}/r$ where α is a

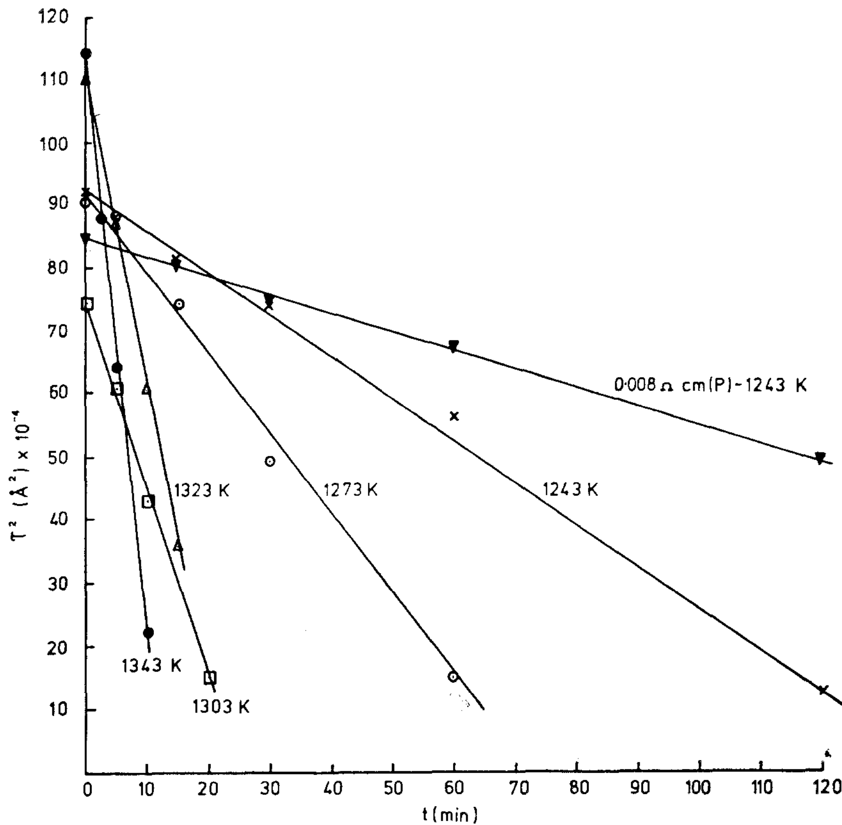

Figure 2 Plot of the square of the loop radius versus annealing time for dislocation loops in 5 Ωcm p-type silicon at various temperatures and in 0.008 Ωcm p-type silicon at 1243 K.

constant. Using values of $G = 7.55 \times 10^{11}$ dyn cm^{-2}, $\sigma = 0.27$ and $B^2 = 12.77 \times 10^{-16}$ cm^2 the value of α varied from 96 at 1070°C to 104 at 970°C. Equation 1 thus reduces to

$$\frac{\mathrm{d}r}{\mathrm{d}t} = -\left(\frac{\pi D_\mathrm{S}}{f_\mathrm{I}\,\boldsymbol{b}\ln(2s/\boldsymbol{b})}\right)\left(\frac{\alpha\boldsymbol{b}}{r}\right) \tag{5}$$

which may be integrated to give a parabolic relationship between loop radius and time.

$$\frac{\mathrm{d}r^2}{\mathrm{d}t} = -\frac{2\pi D_\mathrm{S}\alpha}{f_\mathrm{I}\ln(2s/\boldsymbol{b})}\,. \tag{6}$$

3.2. Vacancy self-diffusion mechanism

If the loop shrinks by vacancy diffusion, the rate of loop shrinkage is given by

$$\frac{\mathrm{d}r}{\mathrm{d}t} = -\frac{\pi D_\mathrm{S}}{f_\mathrm{V}\,\boldsymbol{b}\ln(2s/\boldsymbol{b})}\left[1 - \frac{C_\mathrm{L}}{C_0}\right] \tag{7}$$

and the vacancy concentration C_L in equilibrium with the loop is given by

$$\frac{C_\mathrm{L}}{C_0} = \exp\left(-\frac{\Delta F}{kT}\right)\,. \tag{8}$$

The term in square brackets in Equation 7 approximates to $(\alpha\boldsymbol{b}/r)/(1 + \alpha\boldsymbol{b}/r)$ where α has the same numerical value as before and the rate of loop shrinkage then becomes

$$\frac{\mathrm{d}r}{\mathrm{d}t} = -\left(\frac{\pi D_\mathrm{S}}{f_\mathrm{V}\boldsymbol{b}\ln(2s/\boldsymbol{b})}\right)\left(\frac{a\boldsymbol{b}/r}{1 + \alpha\boldsymbol{b}/r}\right)\,. \tag{9}$$

4. Results

The thin foils containing the dislocation loops were annealed in vacuum at temperatures between 970 and 1070°C and electron micrographs were taken of the same loop after each anneal. Each loop was annealed four or five times and a minimum of five loops were studied for each annealing temperature and doping concentration. A plot of the square of the loop radius as a function of annealing time is shown in Fig. 2 for 5 Ωcm p-type material at different

TABLE I The experimental values of the self diffusion coefficient, D_s (cm^2 sec^{-1}), and the calculated electron concentration, n_D (cm^{-3}), as a function of room temperature resistivity and annealing temperature

Room temperature resistivity (Ω cm)	Annealing temperature (K)									
	1243		1273		1303		1323		1343	
	D_s	n_D	D_s	n_D	D_s	n_D	D_s	n_D	D_s	n_D
0.005 (n)	2.86×10^{-16}	1.76×10^{19}	6.72×10^{-16}	1.84×10^{19}			2.53×10^{-15}	2.02×10^{19}	3.59×10^{-15}	2.12×10^{19}
0.01 (n)	1.58×10^{-16}	9.54×10^{18}	4.28×10^{-16}	1.07×10^{19}	8.77×10^{-16}	1.20×10^{19}	1.68×10^{-15}	1.30×10^{19}	2.19×10^{-15}	1.42×10^{19}
200 (n)	1.02×10^{-16}	6.13×10^{18}	2.45×10^{-16}	7.35×10^{18}	6.16×10^{-16}	8.75×10^{18}			1.59×10^{-15}	1.09×10^{19}
5 (p)	8.95×10^{-17}	6.13×10^{18}	2.00×10^{-16}	7.35×10^{18}	4.85×10^{-16}	8.75×10^{18}	9.33×10^{-16}	9.80×10^{18}	1.35×10^{-15}	1.09×10^{19}
0.01 (p)	6.54×10^{-17}	2.57×10^{18}	1.66×10^{-16}	3.49×10^{18}	4.22×10^{-16}	4.61×10^{18}	6.91×10^{-16}	5.49×10^{18}	1.07×10^{-15}	6.48×10^{18}
0.008 (p)	3.87×10^{-17}	2.08×10^{18}	1.03×10^{-16}	2.86×10^{18}	3.05×10^{-16}	3.86×10^{18}	6.42×10^{-16}	4.65×10^{18}	9.26×10^{-16}	5.55×10^{18}
0.005 (p)	2.50×10^{-17}	1.47×10^{18}	6.88×10^{-17}	2.07×10^{18}	2.25×10^{-16}	2.85×10^{18}	5.36×10^{-16}	3.49×10^{18}	8.42×10^{-16}	4.24×10^{18}

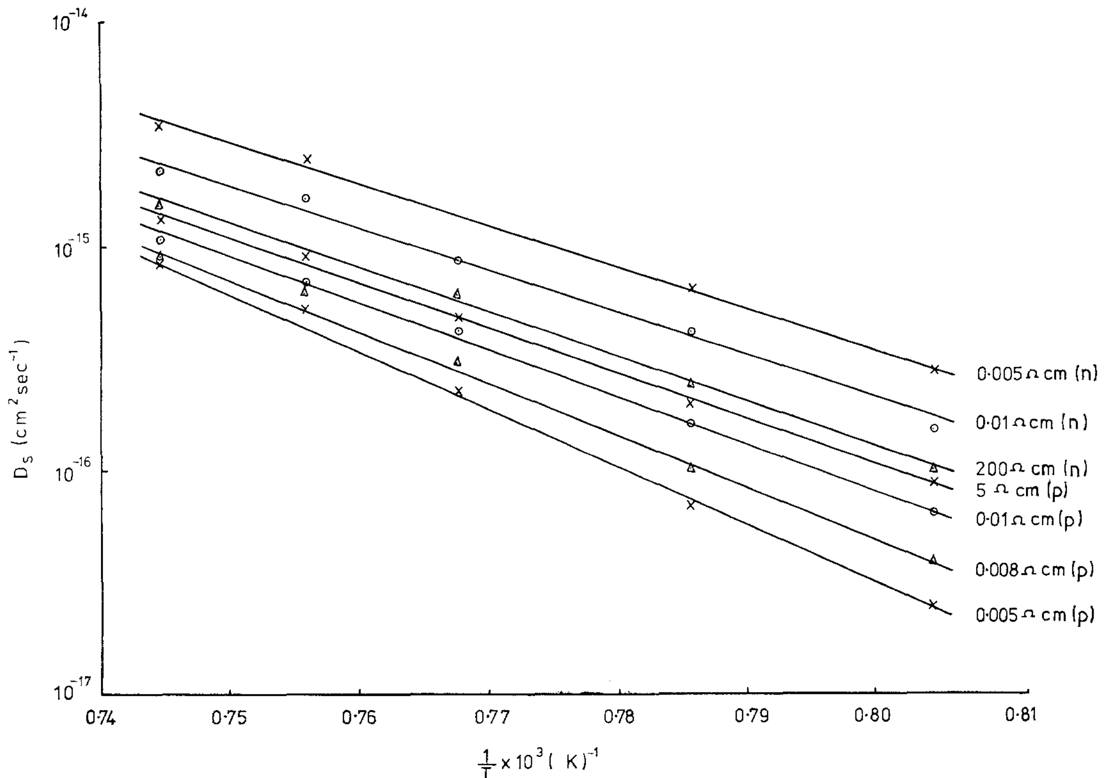

Figure 3 Temperature dependence of the self diffusion coefficient of doped silicon.

annealing temperatures. The data are in accord with Equation 6, and the scatter in the measured slope for different loops annealed in the same material at the same temperature was about 10%.

For a vacancy diffusion mechanism, Equation 9 predicts a divergence from a parabolic relationship but for the range of loop radii used in the present work, this divergence is very small and the experimental results made an equally good fit to both Equation 9 and 6. No conclusions about the diffusion mechanism can, therefore, be drawn from the annealing kinetics.

We have chosen to analyse the results in terms of Equation 6 and the coefficient of self-diffusion D_S was calculated from the slope of the plots of the loop radius squared against annealing time for each specimen resistivity and annealing temperature. This approach is not meant to imply that the diffusion mechanism is of interstitialcy type rather than vacancy type. In fact, if Equation 9 is used to calculate the self diffusion coefficient, the values obtained are only about 10% greater than the values obtained using Equation 6, which is of the same order of magnitude as the experimental scatter in the slope.

The values obtained are given in Table I and are plotted in Arrhenius form in Fig. 3. The results show that for a given temperature the diffusion coefficient is greatest in the heavily doped n-type material and decreases as the degree of n-type doping decreases and the degree of p-type doping increases. The apparent activation energy increases in a similar continuous way from heavily doped n-type to heavily doped p-type material.

5. Discussion

The result that the diffusion coefficient decreases in going from n-type material to p-type material suggests that the point defects responsible for self diffusion are acting as acceptors. Thus in n-type material the effective formation energy of the points defects is reduced by the energy released when an electron drops from the Fermi level to the point defect acceptor level. The total point defect concentration is the sum of the neutral point defect concentration C^0 and the

concentration of negatively charged point defects C^1, i.e.

$$C^1 = 2C^0 \exp(E_F{}^D - E_A)/kT \qquad (10)$$

where $E_F{}^D$ is the Fermi energy of the doped material and E_A is the point defect acceptor energy referred to the top of the valence band. The factor 2, which is erroneously given as $\frac{1}{2}$ in some references, arises from the increased configurational entropy associated with the two possible spin orientations of the occupying electron.

The self diffusion coefficient $D_S{}^D$ in doped material is then given by

$$D_S{}^D = D_S{}^0[1 + 2\delta \exp(E_F{}^D - E_A)/kT)] \qquad (11)$$

where $D_S{}^0$ is the self diffusion coefficient associated with neutral point defects and δ is the ratio of the diffusivities of the charged and neutral point defects. Since the electron concentration n_D in the doped material is related to that in intrinsic material n_I by

$$n_D/n_I = \exp(E_F{}^D - E_F{}^I)/kT \qquad (12)$$

where $E_F{}^I$ is the Fermi energy of intrinsic material, Equation 11 can be written

$$D_S{}^D = D_S{}^0[1 + 2\delta(n_D/n_I) \exp(E_F{}^I - E_A)/kT]. \qquad (13)$$

Values of the intrinsic electron concentration were calculated from the empirical relationship obtained by Barber [11] from an analysis of the results obtained by a number of workers.

$$n_I = 3.1 \times 10^{16} T^{3/2} \exp(-Eg/2kT) \qquad (14)$$

For temperatures greater than 700 K a correction has to be made to the above expression to take account of the decrease in the band gap caused by the electrostatic interaction of the carriers. This was done using the expression given by Morin and Maita [12].

$$Eg = 1.206 - 7.1 \times 10^{-10}(n_I/T)^{\frac{1}{2}} \qquad (15)$$

The electron concentrations in the doped material were then obtained from the electroneutrality relation and are given in Table I.

The value of the measured diffusion coefficient was plotted against n_D/n_I at each temperature and Fig. 4 illustrates the linear relation between these parameters in agreement with Equation 13. In principle, a full analysis of these data would allow $D_S{}^0$ and $\delta \exp(E_F{}^I - E_A)/kT$ to be determined at each temperature, but the intercept (equal to $D_S{}^0$) is small and the scatter on the data points precludes any meaningful determination of this quantity. In fact, a least squares fit analysis gave a small negative intercept for two of the temperatures. The term $\delta \exp(E_F{}^I - E_A)kT$ is given by the slope divided by the intercept and is, therefore, sensitive to errors in the intercept. Apart from the experimental scatter these results may be affected by systematic errors in the electron concentrations. These were calculated using an impurity concentration determined from room temperature resistivity measurements. For the high doping level, it is possible that some impurity is electrically inactive at room temperature due, for example, to precipitation, and thus the concentration of electrically active impurities may be higher at the diffusion temperature than at room temperature.

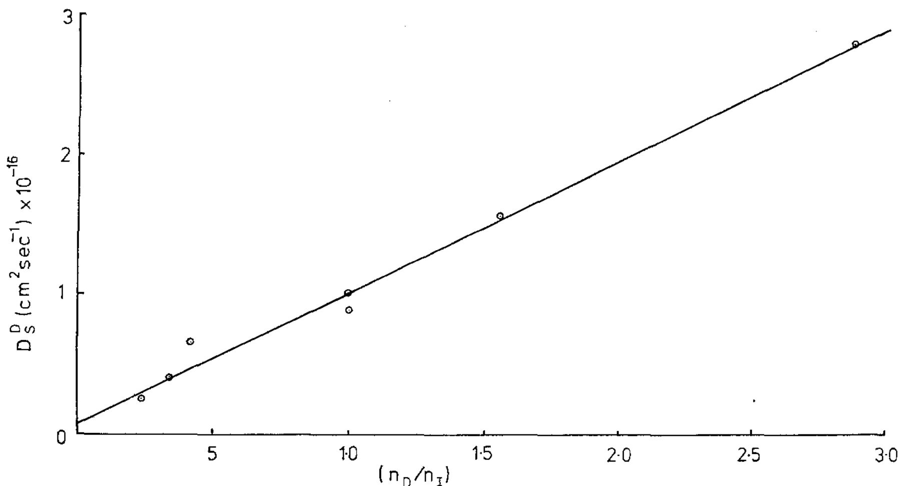

Figure 4 The dependence of the self diffusion coefficient on the electron concentration in silicon at 1243 K.

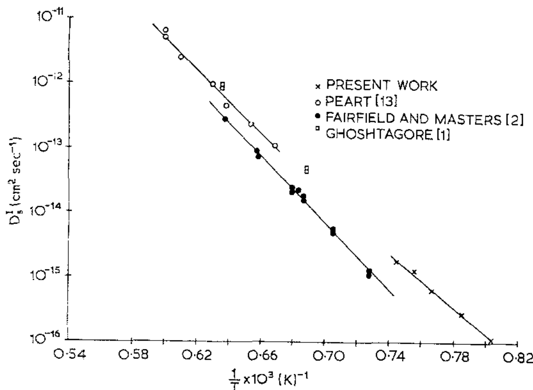

Figure 5 Temperature dependence of the self diffusion coefficient of intrinsic silicon.

This would have the effect of increasing the electron concentration in heavily doped n-typed material and decreasing it in p-type material and thus the slope of the graph would be reduced and the intercept increased. The value of the self diffusion coefficient in intrinsic material can be obtained from Fig. 4, and is insensitive to the possible errors mentioned above because these cause the graph to pivot about this position. The intrinsic self diffusion coefficient was obtained from a least squares fit analysis at each temperature and the results are plotted in Arrhenius form in Fig. 5. An analysis of these results leads to an expression for the self diffusion coefficient in intrinsic material.

$$D_S{}^I = 5.8 \exp(-4.1/kT)$$

The measurements of the self-diffusion coefficient in intrinsic material made by Ghoshtagore [1], Fairfield and Masters [2] and Peart [13] using profiling techniques are also included in Fig. 5 for comparison. The values obtained in the present work are in good agreement with the extrapolated data of Peart and Ghoshtagore and the combination of these three sets of data is suggestive of a curved Arrhenius plot. It has been proposed by Seeger and Chik [14] that the Arrhenius plot is curved because the relative contributions of vacancies and interstitials to diffusion is temperature dependent.

It is not clear why p-type doping has an opposite effect in the present case to that of Fairfield and Masters but the present results are consistent over a wide range of doping concentration and the linear relation obtained between the self diffusion coefficient and the electron concentration clearly support the conclusion that the point defects responsible for self diffusion act as acceptors.

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