Diffusion and Electrical Behavior of Zinc in Silicon

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Zinc has been diffused into Si single crystals and estimations of the diffusion constant and solubility have been obtained by conductivity measurements. In the range 1000–1300°C the diffusivity varies between 10^{-6} and 10^{-7} cm^2/sec. However, no definite trend with temperature could be established, presumably because of surface barriers on the Si. A maximum solubility of about 1.4×10^{17} cm^{-3} occurs at 1350°C and retrograde behavior is observed.

Hall effect and conductivity measurements as functions of temperature have been made on Si crystals containing diffused Zn. One acceptor level only was found for Zn at 0.31 ev above the valence band. B, Ga Al, and As were used as doping impurities. The electronic levels of the doping acceptors were altered by the presence of Zn, suggesting compound formation between the acceptor atoms and Zn.

INTRODUCTION

BECAUSE of the high volatility of zinc at the temperatures (over 1400°C) employed in growing silicon single crystals, it has been difficult to produce crystals containing zinc by the conventional doping procedure. Early attempts to diffuse zinc into silicon showed the rate of diffusion at 1000 to 1300°C to be considerably higher than that found for zinc in germanium at 800 to 900°C.[1] That work also indicated that new electronic energy levels were introduced when zinc was diffused into silicon.[2] The present paper describes experiments in which zinc has been diffused into undoped silicon crystals and into crystals doped with boron, aluminum, gallium, and arsenic. The first part deals with diffusion and solubility, the second part with the electronic energy levels found.

I. DIFFUSION AND SOLUBILITY OF Zn IN Si

Preliminary experiments showed that Zn provides at least one acceptor level[2] in silicon and in this respect behaves like Zn in Ge.[3] In order to investigate the diffusion in Si more completely the method of fractional saturation was employed, the details of which are described below.

A. Basis of the Method

When diffusion takes place into a slab whose broad faces are large in dimensions compared to its thickness, it can be easily shown[4] that the amount of diffusant entering the slab in a time t, divided by the amount which would enter in infinite time, i.e., the fractional saturation, is simply related to the diffusion coefficient. The relation is

$$F = 2.26(Dt)^{\frac{1}{2}}/a, \qquad (1)$$

where F is the fractional saturation in time t, D is the

diffusion coefficient in cm^2/sec, and a is the thickness of the slab in cm. This relation is based on the error function solution and holds only in the case where no appreciable overlapping of the penetration curves from the two sides of the slab occurs, i.e., for fractional saturations in the range up to about 0.6. In (1) it is assumed that the surface concentration is constant all during the diffusion, that the diffusion coefficient is constant independent of concentration, that Fick's laws hold, and that the initial concentration is uniform or zero.[5]

The same relationship holds for the diffusion of a volatile diffusant *out* of a slab in which case one measures the fractional amount of diffusant removed from the slab, i.e., the amount removed or lost in time t divided by the amount which would be lost in infinite time. In this case, the concentration of the slab surface is assumed to be zero or some constant value less than the uniform initial concentration all during the process.

In the present work the amount of diffusant, in this case Zn, entering or leaving the slab was measured by the change in the electrical conductance (measured at room temperature) after successive anneals for known times at fixed temperatures. Since the conductance of the slab is proportional to the number of carriers present multiplied by their mobility, a simple electrical measurement made initially and after a given time of anneal suffices to determine the diffusion coefficient D. Mobilities corresponding to the average resistivities of the specimens have been used in each instance. No corrections for mobility variation over the penetration curve have been made since these are small because of the low Zn concentrations.

The use of conductivities to determine changes proportional to the Zn concentrations requires that a constant number of holes is contributed by each added Zn atom. To insure complete ionization of the Zn, n-type silicon sufficiently doped with arsenic so that it remained n type after saturation was employed. It

[1] W. C. Dunlap, Jr., Phys. Rev. **86**, 615(A) (1952); C. S. Fuller, Phys. Rev. **86**, 136 (1952).
[2] J. A. Burton, Physica **20**, 845–854 (1954).
[3] W. C. Dunlap, Jr., Phys. Rev. **96**, 42 (1954).
[4] *Atom Movements* (American Society for Metals, Cleveland, Ohio, 1951), p. 39.

[5] It is also assumed that diffusion potential and surface potential effects are negligible. This requirement is met since at the high temperatures employed in this work such fields are swamped out by intrinsic carriers.
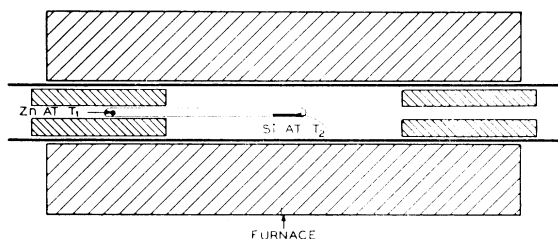
FIG. 1. Method of obtaining precise control of Zn vapor pressure.

appears from Hall measurements (see below) that one hole is provided by each Zn atom under these conditions.

The relation employed to calculate D for the inward and outward diffusions is as follows:

$$D = a^2(\sigma_0 - \sigma_t)^2/5.11t(\sigma_0 - \sigma_\infty)^2. \qquad (2)$$

Here a is the slab thickness in cm, σ_0 is the conductivity at zero time, σ_t that at time t, and σ_∞ at infinite time, i.e., the conductivity corresponding to saturation at the temperature in question for inward diffusion and to entire absence of Zn for the outward diffusion.

B. Procedure

The method employed consisted in heating silicon wafers 1.0×0.4 cm by 0.060–0.070 cm thick in Zn vapor at temperatures between 900 and 1360°C. The Si was arsenic-doped during the crystal growing and ranged in resistivity from about 1.0 to 0.04 ohm cm n type. The diffusions were conducted in sealed quartz tubes which contained the Si specimens together with pure Zn.[6] The latter was regulated in amount to give between 0.5 and 1.5 atmospheres pressure at the diffusion temperature. More precise control of the Zn vapor pressure was obtained in a number of runs by maintaining a temperature gradient in the tubes by an arrangement similar to that shown in Fig. 1. No effects attributable to a change in the Zn vapor pressure were found in these runs, even though the pressure was varied from 7 to 760 mm of Hg. Possible reasons for this are discussed below. Temperatures were controlled to within ±3°C and residual air, He, and H_2 were all separately employed as ambients (at 0.001 mm pressure at 25°C) without finding any effects of the different gases on the results. Outward diffusions were conducted in flowing H_2 or flowing He as well as under continuous pumping at 0.001 mm pressure. Similar diffusion results to those observed in sealed tubes were observed under these conditions. No evidence of a reaction of Zn with the quartz containers was evident even at the highest diffusion temperatures. This is to be expected because of the free energy of formation of the respective oxides.[7]

Saturation runs were made at several temperatures in an attempt to determine a solubility-temperature

curve for Zn. Inasmuch as the duplicate runs differed considerably, even under carefully controlled conditions of temperature and pressure, it was possible to secure only an approximate solubility curve.

All conductivities were determined by means of a two-point probe having 0.635-cm separation. A precision of at least ±1% was obtainable in this measurement.

C. Results

The results of the saturation runs are shown in Fig. 2 which also plots data from Part II to be discussed. Each data point in this figure is the average of 3 to 9 determinations whose spread is indicated by the range line at that point. In calculating the number of holes added (equal to the number of electrons removed), the mobilities for electrons were taken from the work of Prince[8] for the higher resistivities and of Morin and Maita[9] for the lower resistivities. The diffusion results are too scattered to be reported in detail and will be summarized below.

D. Discussion—Diffusion Results

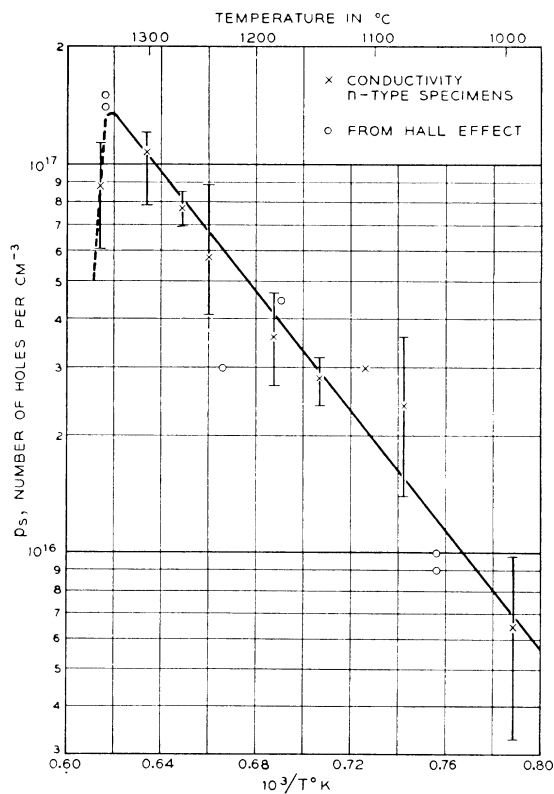All of the diffusion coefficients, whether determined by inward or outward diffusion, and more or less

FIG. 2. Free-hole concentrations as a measure of Zn solubility as it depends upon reciprocal temperature.

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[6] Analysis showed the Zn to be at least 99.999% pure.
[7] J. P. Coughlin, Bulletin of the Bureau of Mines No. 542, 1954.
[8] M. B. Prince, Phys. Rev. 93, 1204 (1954).
[9] F. J. Morin and J. P. Maita, Phys. Rev. 96, 28 (1954).

independently of temperature, fall between about 10^{-6} and 10^{-7} cm² per sec. The average of 30 results for inward diffusion is 6.1×10^{-7} cm²/sec and of 8 results for outward diffusion 4.3×10^{-7} cm²/sec. There appears to be little definite trend with temperature although there is a correlation of higher temperatures with higher diffusion constants. We do not have an explanation for this or for the variability in the diffusion values. That the presence of oxide films on the silicon surface is one factor of importance is indicated by the fact that alloying of the Zn with the silicon specimens was observed in only one instance.[10] This occurred after sealing and during the high-temperature heating period when it is believed one of the specimens fractured, since alloying was observed on the freshly fractured surface only. A variable amount of surface oxide (SiO_2) is also suggested by the outward diffusion experiments in which induction periods for diffusion were observed, as if surface films had to be removed or penetrated before rapid outward diffusion could take place. In view of the inability of Zn to displace oxygen from SiO_2,[7] and as evidenced by the fact that no visible attack of Zn on the quartz containers occurred, even after hundreds of hours heating at 1250°C, it is perhaps not surprising that surface barriers to Zn diffusion are present on silicon.

Another observation which appears to be significant is that the alloying of Zn occurs much more readily on crystals grown with slow-rotation (1.5 rpm) than on those rotated rapidly (100 rpm) during growth. This suggests that the supposed higher oxygen content of the rotated crystals[11,7] may be the cause. Perhaps the latter form surface oxide barriers more readily under the conditions of our experiments than do the slow-rotated crystals. However, no significant difference in diffusion constant or in the consistency of the results was evident for the slow-rotated silicon crystals. Further evidence of a surface barrier for diffusion is provided by the lack of dependence of the diffusion rate on the Zn vapor pressure mentioned earlier.[12]

In most of the diffusion experiments care was taken to avoid errors due to precipitation of Zn by rapid quenching and by diffusing out at temperatures equal to or above those where saturation was carried out. In some experiments in which Zn was diffused out, saturation was at higher temperatures. These runs would be expected to result in lower D values. The large variability in D, however, even for runs in which no precipitation could have occurred, obscures any effect on this kind if it is present. That Zn does not precipitate from silicon at room temperature is shown by the fact that no resistivity changes occur on standing. Even at 450°C little or no precipitation of Zn occurs.

The diffusion rate of Zn in silicon would therefore appear to be low at this temperature.

Summarizing, we may say that the diffusion of Zn in silicon is complicated by the presence of surface barriers, probably SiO_2. The largest diffusion constants are of the order of 10^{-6} cm²/sec, although even these may be subject to some surface restriction. Since values of $D=10^{-6}$ occur at lower temperatures as well as high (although less frequently), no activation energy for the diffusion can be estimated.

E. Discussion—Solubility Results

The curve showing the solubility of Zn as a function of temperature (Fig. 2) appears to have significance in spite of the large errors of the individual determinations. This curve represents the approximate trend of all the data including that described in Part II below. There is a suggestion that a maximum in the solubility curve occurs at about 1300°C corresponding to 10^{17} atoms/cm³ if one acceptor level per atom is assumed.

We have no explanation for the wide variations in solubility for identical temperatures and saturation conditions. It was at first believed that this was a result of variable vapor pressure of the Zn. Several experiments were therefore undertaken in which the vapor pressure was controlled at different levels during diffusion at 1185°C. However, inconsistent results were obtained in these runs. No relation between Zn vapor pressure and solubility could be established although at pressures near 1 atmosphere fairly good duplication was possible. Barrier films on the silicon may again be a factor. Perhaps more careful tests under high-vacuum conditions will show the expected pressure dependence.

Another possible cause of variation may be an interstitial-substitutional equilibrium such as has been proposed for the state of Cu in germanium.[13] This might be expected to depend on the rate of quenching from high temperature. However, no correlation with quench rate, within our ability to control it, could be established, but we were unable to investigate quench times of less than about 5 sec, since these caused fracture of the specimens. The random nature of the solubility variations also suggests that an interstitial-substitutional Zn equilibrium may be a more realistic explanation of their origin.

In connection with Fig. 2 it is interesting to note that the data fit (in the linear portion) the equation

$$p=7.3\times10^{21}\exp-(1.5/kT), \qquad (3)$$

where k is expressed in ev per degree. Since, under the conditions of the experiment, the number of holes is equal to the number of Zn atoms if we assume a single acceptor level (see Part II), relation (3) also gives the

[10] Recent observations on the influence of dislocations on the diffusion of Cu in Ge suggest that variations in crystal perfection may also be a factor.

[11] Kaiser, Keck, and Lange, Phys. Rev. 101, 1264 (1956).

[12] Even cleaning the specimens of rotated silicon by heating to glowing in vacuum did not provide uniform surface alloying of Zn although more local alloying occurred.

[13] F. van der Maesen and J. A. Brenkman, J. Electrochem. Soc. 102, 229 (1955). A. W. Tweet and C. J. Gallagher, Phys. Rev. 103, 828 (1956); C. S. Fuller and J. A. Ditzenberger, Phys. Rev. (to be published).
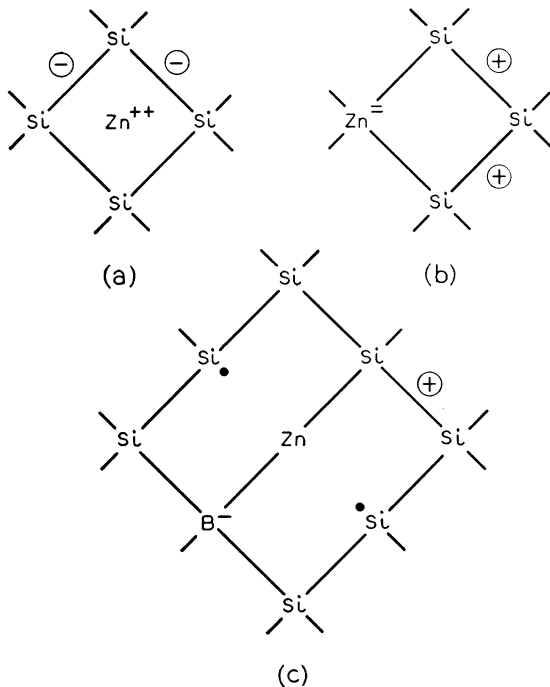
FIG. 3. Schematic diagrams for (a) interstitial Zn atom as a donor, (b) substitutional Zn atom as an acceptor, (c) Zn B compound as an acceptor.

solubility of Zn as a function of temperature. The energy of solution of Zn in Si is then 1.51 ev or 35 kcal. This value lies close to that (27 to 35 kcal) found for Cu in Ge [14] suggesting an analogous solution behavior for these two systems. The dashed line in Fig. 2 represents the extrapolation based on the expected behavior of the Zn-Si liquidus and again is analogous to the curve for Cu in Ge which likewise shows retrograde solubility.

Several saturations were carried out at 1350°C using p-type silicon of different resistivities. The changes observed in the resistivities (measured at room temperature) were small and consistent with a single deep-lying acceptor level (see Part II). These experiments appear to exclude the presence of any appreciable number of donor levels in the upper half of the forbidden gap and would argue against all but small concentrations of interstitial Zn.

II. ELECTRONIC ENERGY LEVELS FROM Zn IN Si

The high diffusion coefficient found for Zn in Si and reported in Part I suggests that the flow of Zn at high temperatures is mainly interstitial. Figure 3(a) illustrates an interstitial Zn atom which would be expected to introduce two donor levels into Si. Since, at low temperature, Zn is found to have introduced acceptor levels into Si, it is assumed that interstitial Zn reacts with lattice vacancies at high temperature to produce substitutional Zn. Figure 3(b) illustrates a substi-

[14] Fuller, Theuerer, and van Roosbroeck, Phys. Rev. 85, 678 (1952); L. Esaki, Phys. Rev. 89, 1026 (1953).

tutional Zn atom which might be expected to introduce two acceptor levels into Si. Thus Zn could conceivably introduce both donors and acceptors into pure Si. Furthermore, in the light of our experience in diffusing Li into Ge,[15] we might expect Zn diffusion into doped Si to produce ion pairs and compounds. Figure 3(c) illustrates a ZnB compound. The compound has empty orbitals and so might act as an acceptor.

Results

Hall effect and conductivity measurements as functions of temperature were made on the samples listed in Table I. Typical carrier concentration curves for some p-type samples are shown in Fig. 4. The samples were diffused to saturation with Zn using the method of Part I. Control sample 347 was known to contain approximately 7×10^{14} cm^{-3} boron before heating as shown in Table I. It was found to contain 8×10^{14} cm^{-3} boron after heating. This indicates that the heating process alone did not introduce an important amount of electrically active impurities.

A. Deep Level

The conductivity results of Part I suggest that a single deep acceptor and no donors are produced when Zn is diffused into Si. Hall effect measurements on As-doped samples 338, 339, and 351 (Group A, Table I)
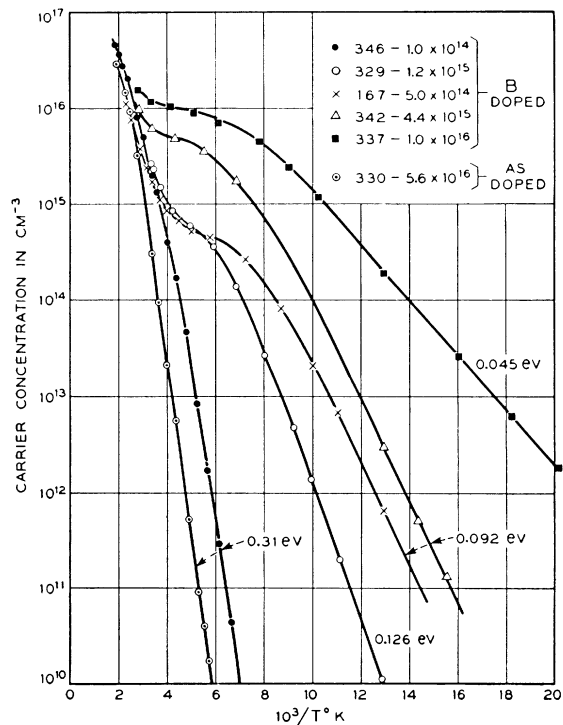

FIG. 4. Carrier concentration curves for a series of silicon samples containing B or As with diffused Zn.

[15] Reiss, Fuller, and Morin, Bell System Tech. J. 35, 535 (1956).

TABLE I. Compilation of Hall effect results on silicon samples before and after diffusion of zinc together with conditions of the diffusion.

Group	Sample No.	Crystal No.	Doping	Amount of doping cm⁻³	Temp. (°C)	Diffusion Time (hr)	Type	Energy levels observed in ev	Amount of shallow levels cm⁻³
A	338	V–909	As	8.7×10^{15}	1070	64	n	0.049 (As)	
	339	V–1041	As	1.7×10^{16}	1070	64	n	0.049 (As)	
	351	V–87	As	4.9×10^{16}	1300	3	n	0.049 (As)	
	334	IV–635	As	2.6×10^{14}	1050	64	p	0.31	
	198	V–13–2	As	2.2×10^{14}	1235	16	p	0.31	
	330	IV–635	As	5.6×10^{15}	1350	2	p	0.31	
B	346	ZR–5	B	1×10^{14}	1350	1.5	p	0.31	
	335	V–218	B	5×10^{14}	1050	16.3	p	0.31, 0.092	9×10^{14}
	336	IV–652	B	1.5×10^{15}	1050	16.3	p	0.31, 0.092	9×10^{14}
	342	V–1172A	B	4.4×10^{15}	1350	1.5	p	0.31, 0.092	4.5×10^{15}
	337	V–834	B	1.0×10^{16}	1350	1.8	p	0.31, 0.092 0.045 (B)	1.0×10^{16}
	333	V–15	B	2.0×10^{17}	1350	2.0	p	0.045 (B)	2.2×10^{17}
C	167	V–218	B	5×10^{14}	1175	64	p	0.31, 0.092	5×10^{14}
	332	V–218	B	5×10^{14}	1350	2	p	0.31, 0.126	4×10^{14}
	357	V–1252	B	1.2×10^{15}	1175	16	p	0.31, 0.092	
	329	V–1252	B	1.2×10^{15}	1350	2	p	0.31, 0.126	6×10^{14}
	356	V–1252	B	1.2×10^{15}	1350	2	p	0.31, 0.126	
D	348	VI–1412	Al	3.5×10^{15}	1350	1.3	p	0.31, 0.078	3.0×10^{15}
	343	V–1029	Ga	7.4×10^{15}	1350	1.3	p	0.31, 0.083	8×10^{15}
	344	VI–469	Ga	3.4×10^{15}	1350	1.3	p	0.31, 0.083	3.2×10^{15}
				Control, no Zn diffused :-					
	347	V–218	B	7×10^{14}	1350	1.3	p	0.045 (B)	8×10^{14}

disclose no new levels in the upper half of the forbidden energy gap. Carrier mobilities indicate scattering only by singly charged centers. Samples 334, 798, and 330 (Group A, Table I), containing As and converted to p-type by Zn diffusion, show a single level at 0.31 ev from the valence band. The curve in Fig. 4 for 330 is typical of these samples. Sample 346, containing 1×10^{14} cm⁻³ B, behaves in the same way. In all other initially p-type samples (Table I) the level after Zn diffusion was also found at 0.31 ev except in sample 333 where it was masked by 2.0×10^{17} cm⁻³ B levels. In these other samples the deep level appears above other levels as shown in the high-temperature range of the curves in Fig. 4.

The concentration of the 0.31-ev level in several samples has been computed from carrier concentration data and the results plotted in Fig. 2. The concentration depends upon diffusion temperature and agrees well with the results of Part I. The concentration was calculated on the assumption that the level is an acceptor associated with substitutional Zn and, therefore, that there are four spin states available in the unionized acceptor for occupation by an electron. Assumption of two spin states would have given results about fifty percent lower in concentration. It is interesting that no second acceptor level comparable to that found for Zn in Ge[3] has been found in the forbidden gap of Si diffused with Zn.
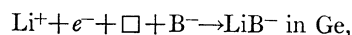
B. Shallow Levels

The results in Table I (Groups B, C, and D) and in Fig. 4 show that new levels are introduced, below the 0.31-ev level and at lower concentrations, by diffusion of Zn into p-type Si. Several facts concerning these levels are to be noted: (a) the level of the original acceptor has disappeared, (b) shallow levels have about the same concentration as the original acceptor, (c) the new level found depends upon the element used for the original acceptor (Group D, Table I), (d) the level depends upon some other (unknown) parameter because both the 0.092 ev and the 0.126-ev levels are found at different times when B is used as the original acceptor. No shallow level is seen in sample 346 containing 1×10^{14} cm⁻³ B. This suggests that the diffusion process adds $\sim 10^{14}$ cm⁻³ donors, perhaps as interstitial Zn, which compensates the level. The 0.092-ev level seems to have a maximum solubility of 5×10^{15} cm⁻³. This behavior is indicated by the curve for sample 337 in Fig. 4. This sample contains 1×10^{16} cm⁻³ B. Analysis of the curve, which shows the 0.045-ev B level, shows the sample to contain $\sim 5 \times 10^{15}$ cm⁻³ of the 0.092-ev level and also $\sim 5 \times 10^{15}$ cm⁻³ of the B level.
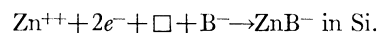
A few conjectures can be made about the nature of the shallow levels. Below a B concentration of $\sim 10^{16}$ cm⁻³ the B level is not observed in the Zn diffused samples. This would not happen if the levels introduced were ordinary acceptors. It would happen, however, if the new levels being added were donors which filled the B levels or if diffused Zn altered in some way the energy of the B levels. If donors were added above the B levels, such donors would be partially emptied according to the concentration of B levels. Carrier concentration curves of these donors would show the

saturation effect corresponding to the B level concentrations. This behavior is observed. However, two facts argue against the levels being donors: (1) their energy depends upon the original acceptor element; (2) calculation of donor and acceptor concentration from carrier concentration curves yields results which do not correspond to the known original acceptor concentration, nor to a donor concentration which would be expected if the new level were associated with substitutional Zn. Hence we conclude that the new levels are probably acceptors and are due to a complex formed between Zn and the original acceptor. We may be dealing with a situation analogous to $Li^{+}+B^{-}$ in germanium[16] where, it is assumed, an ion pair forms and then reacts with a vacancy to form a compound. Thus

$$Li^{+}+e^{-}+\square+B^{-}\rightarrow LiB^{-} \text{ in Ge,}$$

and

$$Zn^{++}+2e^{-}+\square+B^{-}\rightarrow ZnB^{-} \text{ in Si.}$$

The compound shown schematically in Fig. 3(c) would be expected to be an acceptor. The changes in energy level found when Al and Ga are substituted for B seem consistent with the assumption of compound formation. The appearance at different times of two shallow levels when B is used as the acceptor suggests that the situation is even more complicated than has been suspected and that a more careful study must be made of the temperature dependence of equilibria involving substitutional and interstitial Zn, ion pairing, and compound formation.

[16] Reiss, Fuller, and Pietruszkiewicz, J. Chem. Phys. **25**, 650 (1956).

Formation of Ion Pairs and Triplets between Lithium and Zinc in Germanium

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This paper is a study of ion pairs and triplets formed between zinc and lithium dissolved in single crystal germanium. As in earlier work on ion pairs involving simpler acceptors, the effects of ion complexes on Hall mobility, and impurity energy levels have been investigated. Relaxation-time experiments have also been performed. The theoretical analysis of the results is in complete accord with the idea that zinc provides two energy levels for electrons in the forbidden gap.

1. INTRODUCTION

THE formation of ion pairs in germanium and silicon has been discussed in detail in a recent paper.[1] The occurrence of pairs involving the donor lithium and singly charged acceptors such as gallium, aluminum, indium, and boron has been demonstrated experimentally. With the exception of its influence on the diffusivity of lithium, zinc, as an acceptor, was not investigated in any of these experiments. Nevertheless zinc is an especially interesting acceptor since, according to Tyler and Woodbury,[2] it is doubly charged when ionized, possessing energy levels at 0.03 and 0.09 ev above the valence band. This fact is supported by the diffusion data, mentioned above, which show zinc to be orders of magnitude more efficient than the other acceptors in reducing the diffusivity of lithium.

In this article the further investigation of zinc will be described and it will be seen that all measured phenomena associated with ionic interaction are in accord with the existence of two energy levels. Along with pairing, triplet formation is possible when doubly charged ions are involved. This subject will be discussed in the following section.

2. TRIPLETS

In another context the problem of triplets has been considered before by Fuoss and Kraus[3] who examined the interaction of two similar singly charged ions with a third singly charged ion of opposite sign. The triplet so constituted bore a net charge. We shall consider the interaction of two singly charged positive lithium ions with one doubly charged negative zinc. Since this triplet is neutral, the phenomena associated with it are quite different from those of the charged triplet.

Two stages of reaction may be distinguished. In the first a charged pair involving one lithium and one zinc is formed:

$$Li^{+}+Zn^{=}=[Li^{+}Zn^{=}]. \qquad (2.1)$$
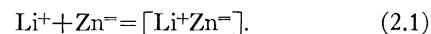
[1] Reiss, Fuller, and Morin, Bell System Tech. J. **35**, 535 (1956).
[2] W. W. Tyler and H. H. Woodbury, Phys. Rev. **100**, 1259(A) (1955).
[3] R. M. Fuoss and C. A. Kraus, J. Am. Chem. Soc. **55**, 2387 (1933).