PHYSICAL REVIEW VOLUME 108, NUMBER 6 DECEMBER 15, 1957

Double-Acceptor Behavior of Zinc in Silicon

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(Received August 19, 1957)

Zinc has an acceptor level at 0.31 ev from the valence band as noted by Fuller and Morin. Under proper doping conditions, another level is observed at 0.55 ev from the conduction band in *n*-type silicon samples into which zinc has been diffused. Gold, manganese, and iron, however, have levels close to 0.55 ev. Gold is eliminated as an interfering impurity on the basis of neutron activation analysis. Manganese and iron are unlikely to be present in high enough concentrations on the basis of their electrical activity in samples deliberately doped with these elements. Mobility and radioactive solubility studies tend to confirm the hypothesis that the 0.55-ev level represents a second acceptor level associated with zinc.

INTRODUCTION

ZINC exhibits acceptor behavior when diffused into *n*-type silicon. Fuller and Morin[1] identified an acceptor level at 0.31 ev from the valence band from the temperature dependence of resistivity and Hall coefficient. Other levels closer to the valence band were found when zinc was diffused into *p*-type silicon. Their level positions depended upon the Group III acceptor present (boron, aluminum, or gallium) so they attributed these levels to complex ion formation between zinc and the shallow acceptor. They observed no levels above the center of the forbidden band.

If the 0.31-ev level arises from zinc in a substitutional position in the lattice, then it is likely that zinc (with $4s^2$ electron configuration as the neutral atom) would accept an additional electron to complete tetrahedral bonding to the neighboring silicon atoms. There would then be another acceptor level observable under the right condition, namely, that the donors present in the silicon be sufficient to provide one electron to each of the zinc atoms but not sufficient to provide two electrons for all the zinc atoms. Such a double acceptor action has been observed by Tyler and Woodbury[2] for zinc in germanium, but has not been found for any of the impurities thus far studied in silicon (iron, manganese, gold, or copper). Since zinc can be readily diffused into silicon with a reasonably high solubility, a careful search was made for a double acceptor level.

PROCEDURE

Zinc of 99.999% purity was obtained from Johnson Matthey and Company. Milligram quantities of the element were alloyed to silicon samples of $3\times3\times10$ mm^3 size and sealed-off in quartz tubes. The silicon used for these samples was taken from crystals which were pulled from a quartz crucible melt under conditions of zero or very slow rotation. These samples, in control tests, did not show any changes in electrical properties on heat treatment at high temperatures (1000°–1300°C). Following a period in a furnace, the quartz tubes were quenched in water. After etching the sample surfaces, pressure contacts were made to gold or rhodium plated areas; in some cases more nearly ohmic contacts were provided by sparking gold wire containing antimony or boron to the sample. The magnetic field used was 6000 gauss.

ELECTRICAL MEASUREMENTS

Preliminary experiments confirmed the 0.31-ev level and established the 1200°C solubility of electrically active zinc as greater than 2×10^{16} cm^{-3}. Then a section of a phosphorus-doped crystal was selected which had a net donor concentration of 2×10^{16} cm^{-3}. Samples were cut along the direction of the crystal axis to obtain many similar samples. Zinc was diffused into these samples at temperatures ranging from 1040° to 1200°C, as listed in Table I. For the lowest temperatures, the samples remained *n* type with the phosphorus level. For the highest temperature, the 0.31-ev level was measured. For samples held at temperatures of ~1080°C, electrical measurements revealed a new level at 0.55 ev. The samples at ~1100°C had anomalous slopes of ~0.36 ev when resistivity ρ and Hall coefficient R_H were plotted against inverse temperature. In these latter samples the concentration of zinc is close to that of the original donor while the donor concentration varies along the sample length. Figure 1 is a plot of R_H *vs* $1/T$ for a number of the samples.[3]

The 0.55-ev level is close to those reported for iron,[4] manganese,[5] and gold[6] in silicon. Even though only milligram quantities of high-purity zinc were used, the possibility that one of these impurities[7] (or some other element) had given rise to the 0.55-ev level could not be immediately excluded. If the 0.55-ev level could be shown to be present in the same concentration as the 0.31-ev level, however, then the case for a zinc double-acceptor level would be stronger. To this end, the low-

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[1] C. S. Fuller and F. J. Morin, Phys. Rev. **105**, 379 (1957).

[2] W. W. Tyler and H. H. Woodbury, Phys. Rev. **102**, 647 (1956).

[3] The values given in Fig. 1 for the slopes are not corrected for the $T^{\frac{3}{2}}$ dependence of states at the conduction or valence band edges. Such corrections would reduce those values by ~0.02 ev.

[4] C. B. Collins, Bull. Am. Phys. Soc. Ser. II, **1**, 49 (1956).

[5] R. O. Carlson, Phys. Rev. **104**, 937 (1956).

[6] Collins, Carlson, and Gallagher, Phys. Rev. **105**, 1168 (1957).

[7] Johnson Matthey's analysis of zinc lot stated <0.001% Fe present with no spectroscopic evidence for Au or Mn.

TABLE I. Zinc-doped silicon samples. Source of all samples was Sec. 3 of crystal C-Si-381.

Sample number	Diffusion T°C	Diffusion Time-hr	Sample Type	Sample Ionization energy	ρ	300°K values R_H	300°K values n	N_{Zn} assuming 2 holes/atom
301	1110	23.5	n	0.05	0.33	310	2.0×10^{16}	0 (control)
296	1045	17.5	n	0.05	0.36	325	1.9×10^{16}	$\sim1\times10^{15}$
319	1053	40	n	0.05	0.92	700	8.3×10^{15}	5.7×10^{15}
320	1065	65	n	0.05	1.54	1050	5.7×10^{15}	7.2×10^{15}
321	1090	18	n	0.05	4.63	2150	2.9×10^{15}	8.5×10^{15}
322	1085	42	n	0.55	1.2×10^{4}	5.8×10^{6}	...	$>1\times10^{16}$
305	1080	64	n	0.55	2.7×10^{4}	1.1×10^{7}	...	$>1\times10^{16}$
302	1110	23.5	p	$\sim$0.36	1.2×10^{3}	2.2×10^{5}	...	$>1\times10^{16}$
306	1100	19	p	$\sim$0.36	1.1×10^{3}	1.6×10^{5}	...	$>1\times10^{16}$
295	1200	17.5	p	0.31	2.6×10^{2}	5.0×10^{4}	...	$>2\times10^{16}$

resistivity n-type samples were studied above room temperature. Sample 296 was excluded because it was not diffused as long as the others and might not be saturated. Sample 321 was excluded because one end of the sample was of appreciably higher resistivity than the other. Samples 319 and 320 were reasonably homogeneous and Hall data on these samples as well as control sample 301 are shown in Fig. 2. The ionization of a deep level occurs in the temperature range from ~425°K to the onset of dominant intrinsic conduction at ~600°K. For sample 319 in which the number of added compensating positive charges is 1.2×10^{16} cm^{-3}, the deep-level concentration is $\sim0.3\times10^{16}$ cm^{-3}; for sample 320 the corresponding concentrations are 1.4×10^{16} and 0.5×10^{16} cm^{-3}. In each case, the deep-level concentration is somewhat lower than one would expect for the double-acceptor hypothesis. However, a deep level close to the middle of the band gap would not be completely ionized when intrinsic conduction begins to dominate. Alternatively, with a model of singly charged zinc centers, one would have to account for concentrations of 0.55 ev, $\sim5\times10^{15}$ cm^{-3}, as arising from impurities in the zinc.

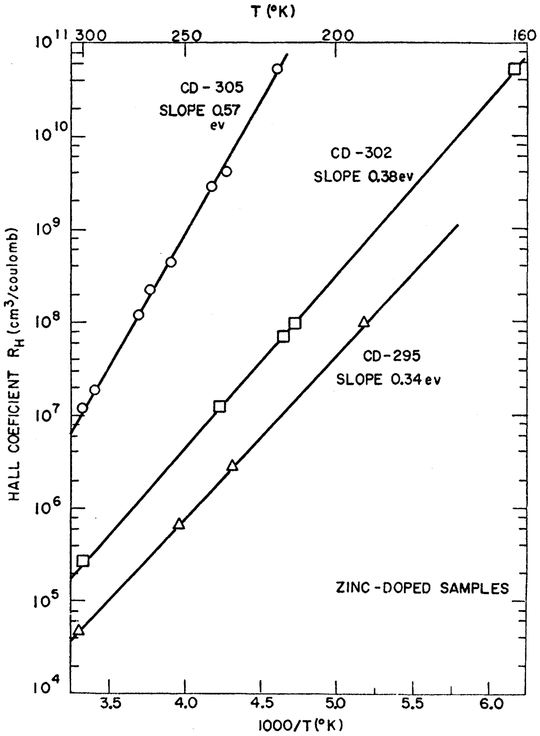

FIG. 1. Hall coefficient *versus* reciprocal temperature for several zinc-doped samples with deep levels. CD-305 was n type, the other two p type.

A neutron activation analysis[8] revealed that less than 10^{15} gold atoms/cm^3 were present in samples 301, 319, 322, and 295. Hence gold can be ruled out as an impurity in zinc responsible for the 0.55-ev level. The electrical activity of Mn in silicon[5] has never been made more than 10^{15} cm^{-3} at 1200°C in diffused samples, even with rapid quenching. At lower temperatures, the solubility is lower so Mn can also be ruled out as the

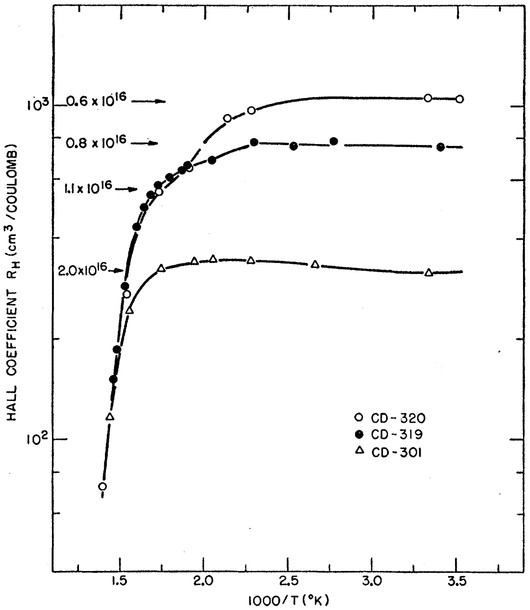

FIG. 2. Hall coefficient *versus* reciprocal temperature in the near-intrinsic range for several low resistivity n-type samples. At lower temperatures, the samples all show the 0.045-ev level characteristic of phosphorus.

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[8] This analysis was carried out by Miss B. Thompson of the General Engineering Laboratory.

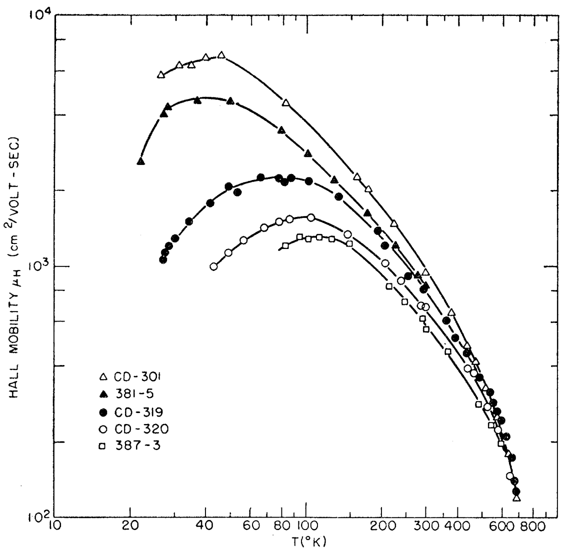

FIG. 3. Hall mobility *versus* temperature for several of the zinc-doped silicon samples and several undoped n-type samples. In sample 381–5, the donor concentration N_D is 4.0×10^{16} cm^{-3}; in 387–3, N_D is 1.5×10^{17} cm^{-3}.

0.55-ev level impurity. The electrical activity of Fe in silicon[4] has been observed to be as high as 2×10^{16} cm^{-3} at 1200°C after a rapid quench; for a slower cooling, such as the zinc samples received in their sealed tubes, only $\sim10^{15}$ cm^{-3} were observed. At 1060°C it is unlikely that the total solubility of iron could be as high as 5×10^{15} cm^{-3} and the electrically active phase should be much less. In all iron-doped samples, heat treatment at 300°C was sufficient to cause loss of all the electrical activity of iron, whereas samples 319 and 320 were raised over 400°C with no measurable change in room temperature concentrations. Furthermore, a ternary system of Zn, Fe, and Si may be established on the silicon surface which would tend to reduce the solubility of iron in the bulk silicon. Such an effect was observed by Thurmond and Logan[9] for copper in germanium using Pb, Sn, In, or Au as the third element.

Further study was made of the mobility of charge carriers in the low ρ, n-type samples. Hall mobility is plotted in Fig. 3 for two zinc-doped samples and several undoped samples in the 10^{16}–10^{17} cm^{-3} concentration range. Calculations were made of the ionized impurity scattering mobility μ_I by using the Brooks-Herring equation.[10] For the zinc-doped samples, μ_I was calculated in one case under the assumption that only singly-charged zinc was present, and in a second case, under the assumption that half as many zinc atoms were present but each was doubly-charged. Since Coulomb scattering is proportional to the square of the charge, the total scattering effect of the zinc ions is twice as great in the second case as in the first. The μ_I was combined with lattice scattering mobility μ_L by using the graph of Conwell.[11] For temperatures above 150°K, the effect of neutral impurity scattering could be neglected. Comparison of the calculated mobilities with measured Hall mobilities indicated a better fit when the acceptor action of zinc in samples 319 and 320 were assumed to arise from doubly-charged rather than from singly-charged centers.

RADIOACTIVE ZINC SOLUBILITY

Samples of silicon were coated with radioactive zinc chloride obtained from the Oak Ridge National Laboratory. After periods at 1200°C in sealed-off tubes, as given in Table II, the surfaces of the samples were ground and etched to remove the surface layers. Counts on the gamma activity of zinc-65 in the samples and in the original $ZnCl_2$ solution and analysis of the total zinc in solution determined the total zinc content of the samples. Some samples were further ground and recounted to insure that the samples were saturated. For the size of our tubes, 1 mg of zinc should give a vapor pressure of about an atmosphere at 1200°C so that the erratic results for the samples with only 0.12 mg zinc present are probably due to insufficient zinc in the tube. The values for samples 271 and 272 are the most reliable and give a solubility of 3×10^{16} cm^{-3}, with an estimated error of ±20%. This solubility agrees with the values observed from electrical measurements and indicates that all of the zinc present is electrically active. But more significantly, this solubility of 3.0×10^{16} cm^{-3} is considerably below the value obtained by Fuller and Morin[1] from electrical measurements assuming only one acceptor state per zinc atom.[12] The dis-

TABLE II. Radioactive zinc diffused into silicon. Mass of zinc given is amount sealed in tube with silicon sample.

Sample number	Mass zinc mg	Time in hours at 1200°C	Measured zinc concentration cm^{-3}
255	0.12	15.7	9.3×10^{15}
256	0.12	23.6	5.7×10^{15}
257	0.12	135.6	4.4×10^{15}
261	0.12	2.3	2.0×10^{15}
269	1.2	15.3	2.0×10^{16}
270	1.2	20.2	2.0×10^{16}
271	3.0	17.1	2.7×10^{16}
272	12.2	17.1	3.0×10^{16}

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[9] C. D. Thurmond and R. A. Logan, J. Phys. Chem. **60**, 591 (1956).

[10] H. Brooks in *Advances in Electronics and Electron Physics*, edited by L. Marton (Academic Press, Inc., New York, 1955), Vol. 7, p. 158.

[11] E. M. Conwell, Proc. Inst. Radio Engrs. **40**, 1327 (1952).

[12] Most of the solubility data of Fuller and Morin derive from conductivity measurements of partially compensated n-type silicon. Some data points, however, were based on Hall effect measurements on samples with the 0.31-ev level. The ratio of zinc acceptors to residual donors was calculated from the shift of Fermi level with temperature assuming a degeneracy factor of four. Even on a simple valence-band model, a factor of two (as given by reference 10, p. 126) would seem more justifiable and would halve their plotted points. E. O. Kane (private communication) pointed out that if the degeneracy of the valence band of silicon is taken into account, the degeneracy factor is $\frac{3}{2}$.

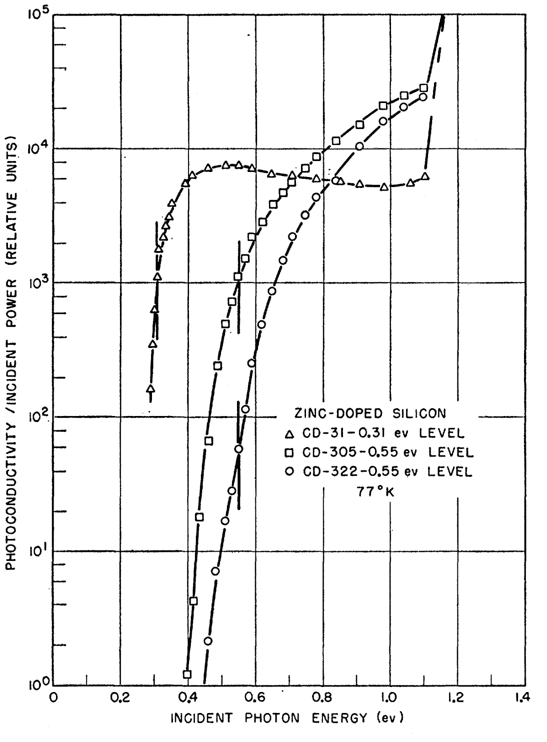

FIG. 4. Photoconductive spectra of p- and n-type zinc-doped silicon crystals are shown. Thermal ionization energies are indicated for comparison with the optical curves. The curves are normalized at 1.16 ev.

crepancy may be due to the large errors inherent in the electrical conductivity measurements or could be largely resolved by assuming that there are two acceptor states per zinc atom and the electrical data should be halved.

OTHER LEVELS

The level at 0.09 ev from the valence band described previously was observed for zinc diffusion in p-type boron-doped silicon of concentrations in the range 10^{15}–10^{16} cm^{-3}. This level was not observed at concentrations over 10^{16} cm^{-3} so that it cannot arise from the same center as the acceptor levels. When the boron concentration was below 10^{15} cm^{-3}, the introduction of zinc by diffusion at 1200°C gave rise to a 0.20-ev level. Since the 0.20-ev level is observed only when the ratio of zinc concentration to net shallow acceptor concentration is very large ($\sim$100) it may not represent a true level but rather a "locking in" of the Fermi level halfway between the 0.31-ev and 0.09-ev levels. The 0.20-ev level could be converted to a 0.13-ev level by heating at 500°C or at 1200°C. This complex of levels may arise from interstitial zinc donors of low solubility, or from interactions of zinc donors with boron acceptors to form ion pairs.[1,13]

OPTICAL STUDIES

The photoconductive spectra as measured by R. Newman are shown in Fig. 4. The 0.31-ev level is supported by the optical threshold. There is no sharp cutoff for the samples with the 0.55-ev levels.[14] Samples in which the 0.20-ev level was observed electrically showed similar spectra to the samples with the 0.31-ev level.

CONCLUSIONS

Evidence has been presented to show that zinc acts as a double-acceptor impurity with levels at 0.31 ev from the valence band and 0.55 ev from the conduction band. This evidence is based on the following: (1) existence of a 0.55-ev level when the condition for observation of a double-acceptor level is satisfied ($2N_{\mathrm{Zn}}>N_{\mathrm{donor}}>N_{\mathrm{Zn}}$); (2) freeze-out of a deep level in partially compensated low-resistivity n-type samples, showing that $\sim\frac{1}{3}$ of the compensating acceptors are in a level just above the middle of the band gap; (3) mobility studies of such n-type samples which suggest ionized-impurity scattering from doubly-charged rather than from singly-charged centers; and (4) comparison of solubility from radioactive zinc studies and from electrical measurements.

Possible contaminating impurities in the zinc which also have $\sim$0.55-ev levels are gold, manganese, and iron. The first is eliminated by neutron activation analysis, the other two on the basis of their limited electrical activity in silicon deliberately doped with these elements and their solubility reduction by formation of a surface terniary system with zinc and silicon.

ACKNOWLEDGMENTS

I am indebted to G. Brower, J. Sobieski, and R. Thomas who carried out many of the experimental measurements, and to W. W. Tyler for valuable suggestions on the experimental details. The early phases of this study were carried out jointly with C. B. Collins.

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

[14] The lack of a sharp cutoff is also evident in the spectra of the deep levels of copper and gold.